

Technical Background Document:
Mercury Wastes
Evaluation of Treatment of Mercury Surrogate Waste
Final Report

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Evaluation of Treatment of Mercury Surrogate Waste

Executive Summary

The Environmental Protection Agency (EPA) and Department of Energy (DOE) have collaborated on a series of studies to evaluate the effectiveness of treatment technologies at stabilizing wastes containing large concentrations of mercury. The study described in this report was designed to provide data to EPA on stabilization of high-mercury subcategory waste sludges (wastes containing greater than 260 mg/kg total mercury) that contain multiple forms of mercury. The data gathered from this treatment demonstration should then provide EPA with information to support a potential revision of current regulations to allow a stabilization alternative of all high-mercury subcategory wastes.

The study evaluated the effectiveness of four technologies at stabilization of mercury in a 'difficult-to-treat' mercury-containing waste, representative of the wide range of such wastes that would require treatment. A surrogate waste was designed for the study, which included an organic form of mercury, elemental mercury, and several mercury salts in an inorganic matrix. The surrogate waste was treated by each vendor, and the treated waste forms evaluated for mercury leachability, using both the TCLP and a novel, automated, constant-pH leaching protocol. Constant pH leaching was conducted at pH 2, 4, 6, 8, 10, and 12 for 14 days at each pH.

The report provides descriptions of the study plan and the treatment processes, as well as detailed discussions of the leaching results. The leaching data presented demonstrate that the stability of the mercury in the treated waste forms varies widely across the pH range tested. Clearly, the stability of mercury in these treated waste forms will be highly dependant on the disposal conditions. The combination of site-specific disposal conditions and appropriate treatment technology must be considered as decisions are made about disposal of waste mercury.

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1. Introduction

The Hazardous and Solid Waste Amendments (HSWA) to the Resource Conservation and Recovery Act (RCRA) require the EPA to establish treatment standards for all listed and characteristic hazardous wastes destined for land disposal. After the effective date of a restriction, wastes that do not meet the Land Disposal Restrictions (LDR) treatment standards are prohibited from land disposal.

The LDR treatment standards for the six waste codes (D009, K071, K106, P065, P091, and U151) which contain mercury as the primary hazardous constituent (Mercury Wastes) were promulgated in the Third LDR Rule (55 FR 22520, June 1, 1990). Some of these standards were revised when EPA promulgated Universal Treatment Standards in the Phase II LDR Rule (59 FR 47980, September 19, 1994). Since these rules were promulgated, however, the Agency has become aware of information and data which indicate that the treatment standards for some categories of these wastes may be inappropriate and warrant further review.

1.1 Disposal Options for Wastes Containing > 260 mg/kg Total Mercury

Under the existing LDRs, treatment by stabilization and disposal is not an available option for most wastes containing greater than 260 mg/kg total mercury (high mercury wastes). The reasons given in the 3rd LDR rule for this regulation are that, "EPA's data for untreated mercury wastes being retorted/roasted domestically show minimum concentrations of mercury up to 255 mg/kg," and that "There is a strong preference in the land disposal restrictions legislation for treatment standards to be based on recovery where possible." The technical background document for mercury wastes also cited data from attempts to treat K106 sludge containing 25.9 g/kg of total mercury using conventional metal-stabilizing agents (cement, kiln dust, lime/fly ash), indicating that the leachability of the waste was actually increased by the process.

In light of EPA's current recognition of mercury as a high priority pollutant and efforts to reduce mercury consumption wherever possible and take mercury out of circulation to minimize air emissions, it appears that the general preference for recovery over immobilization may not be appropriate for some categories of mercury wastes. In addition, various commenters and petitioners have submitted data indicating that wastes containing concentrations well above 260 mg/kg may be effectively stabilized. Therefore, EPA decided to revisit the issue of mercury stabilization by gathering performance data on waste forms produced by commercially available treatment technologies.

1.2 Wastes Which Are Not Directly Amenable to Roasting and Retorting. Retorting or roasting for recovery (RMERC) is currently required for inorganic high mercury wastes. Commenters and petitioners have asserted that many subcategories of mercury wastes (e.g., inorganic salts, corrosive wastes, incineration residues, wastewater treatment residues) are not directly amenable to RMERC treatment, and are not accepted by commercial retorting facilities. Although EPA's general position has been that those nonamenable subcategories can be pretreated to make recovery possible, current management practices indicate that this position may be impractical and unrealistic. Therefore, EPA decided to investigate alternative treatment technologies to roasting and retorting for high-mercury

wastes.

1.3 Incineration of Mercury Wastes

Incineration (IMERC) is currently either required or allowed as an alternative to RMERC for organic high mercury wastes. The rationale for this standard given in the 3rd rule is that IMERC will destroy the organic component of organo-mercury complexes or mixtures, so that the “valuable mercury” present in the waste can be subsequently recovered from the incineration residuals (e.g., ash, baghouse dust, sludge from treated scrubber water). However, given the high volatility of mercury, it is reasonable to assume that both mercury and organo-mercury compounds will be vaporized by incineration rather than remaining in the ash. Although some of this mercury will be captured by air pollution controls, the rest will be lost to the atmosphere. Furthermore, evaluation of current waste management practices indicates that incineration residuals are in fact not being treated for mercury recovery. Therefore, the Agency has decided to further investigate whether treatment alternatives exist for mercury wastes that might currently be going to incinerators for treatment.

The Surrogate Waste Project Report

The purpose of this report is to provide data to EPA on stabilization of high-mercury subcategory waste sludges, that contain multiple forms of mercury. The data gathered from the demonstration of treatment of this sludge should then provide EPA with information to support a potential revision of current regulations to allow a stabilization alternative of all high-mercury subcategory wastes.

2. Background

The Resource Conservation and Recovery Act (RCRA)¹ defines several categories of mercury wastes, each of which has a defined technology or concentration-based treatment standard, or universal treatment standard (UTS). RCRA defines mercury hazardous wastes as any waste that has a TCLP value for mercury of 0.2 mg/L or greater. Three of these categories, all nonwastewaters, fall within the scope of this report on new technologies to treat mercury-contaminated wastes:

- Wastes as elemental mercury
- Hazardous wastes with less than 260 mg/kg [parts per million (ppm)] mercury
- Hazardous wastes with 260 ppm or more of mercury

2.1 Current Treatment Methods

While this report deals specifically with the last category—hazardous wastes with 260 ppm or more of mercury—the other two categories will be discussed briefly so that the full range of mercury treatment challenges can be understood. The treatment methods for these three categories are as follows:

- Waste as elemental mercury—RCRA identifies amalgamation (AMLGM) as the treatment standard for elemental mercury contaminated with radioactive materials.
- Waste with < 260 ppm mercury—No specific treatment method is specified for hazardous wastes containing <260 ppm. However, RCRA regulations require that such wastes that exceed a TCLP mercury concentration of 0.20 mg/L be treated by a suitable method to meet the toxicity characteristic leaching procedure (TCLP)² limit for mercury of 0.20 mg/L.
- Waste with \geq 260 ppm mercury—For hazardous wastes with mercury contaminant concentrations \geq 260 ppm *and* RCRA-regulated organic contaminants (other than incinerator residues), incineration or retorting (IMERC or RMERC) is the treatment standard. For wastes with mercury contaminant concentrations \geq 260 ppm that are inorganic, including incinerator and retort residues, RMERC is the treatment standard.

Hazardous waste contaminated with \geq 260 ppm mercury is the primary focus of this report.

¹ 40 CFR 268.40

² This procedure is described in Method 1311 of U.S. Environmental Protection Agency (EPA) Publication SW-846.

EPA's hazardous waste classification system identifies six categories of mercury-bearing wastes, each of which has a separate RCRA waste code. **Table 2-1** shows the six mercury waste codes and a brief description adapted from the May 28, 1999 proposed rule:

Table 2-1
RCRA Waste Codes for Wastes that Contain Mercury

| Waste Code | Description |
|--|---|
| D009—Characteristic Mercury Wastes | D009 wastes are extremely variable in composition, and depend on the industry and process that generate the waste. Some of the more common types of D009 wastes include miscellaneous wastes from chlor-alkali production facilities (especially cell room trench sludge and activated carbon for liquid or gas purification), used fluorescent lamps, batteries, switches, and thermometers. D009 wastes are also generated in the production of organomercury compounds for fungicide/bactericide and pharmaceutical uses, and during organic chemicals manufacturing where mercuric chloride catalyst is used. |
| K071—Brine purification muds from the mercury cell process in chlorine production, where separately prepurified brine is not used | K071 wastes are generated by the chlor-alkali industry in the mercury cell process. In this process, sodium chloride is dissolved to form a saturated brine solution. The brine solution is purified by precipitation, using hydroxides, carbonates, or sulfates. The precipitate is dewatered to form K071 wastes, while the purified brine continues in the process. The depleted solution from the mercury cell is ultimately recycled to the initial step of the process. |
| K106—Wastewater treatment sludge from the mercury cell process in chlorine production | Like K071 wastes, K106 wastes are generated from chlorine production using the mercury cell process. Effluent from the mercury cell includes spent brine, a portion of which is recycled and a portion of which is purged to wastewater treatment. Other plant area wastewaters (e.g., stormwater, washdown waters) are also typically sent to this treatment system. The wastewater treatment process generates a sludge through precipitation and filtering, which is K106 waste. The mercury concentration in K106 waste is consistently greater than 260 mg/kg and therefore retorting is a required technology for this waste. |
| P065—Mercury fulminate | P065 wastes consist of discarded mercury fulminate product, off-specification mercury fulminate product, and container or spill residues thereof. |
| P092—Phenylmercury acetate | P092 wastes consist of discarded phenylmercury acetate product, off-specification phenylmercury acetate product, and container or spill residues thereof. |
| U151—Mercury | U151 wastes consist of discarded elemental mercury product, off-specification metallic mercury product, and container or spill residues thereof. The principal constituent of U151 is metallic mercury. |
| <p>* U.S. EPA, Best Demonstrated Available Technology (BDAT) Background Document for Mercury Wastes, Nov 1989, page 2-18.</p> <p>** Mercury Treatment and Storage Options Summary Report, A.T. Kearney report for USEPA Reg 5, May 1997, page 1.</p> | |

2.2 Mixed Waste (RCRA and Atomic Energy Act (AEA))

Mixed waste is waste that contains both hazardous chemical components, subject to the requirements of RCRA, and radioactive components, subject to the requirements of the Atomic Energy Act. Mercury-contaminated low-level radioactive waste (LLW) is considered mixed waste and is therefore regulated by both EPA and the U.S. Nuclear Regulatory Commission (NRC). Given the combined restrictions of both EPA and NRC, there is no disposal path available for mixed waste. Since the radioactive characteristic cannot be eliminated, mixed wastes must be treated to eliminate

the hazardous characteristic so that they may then be disposed of in accordance with NRC regulations.

Treatment requirements for radioactive mercury-contaminated LLW (D009 as designated by EPA) are governed by 40 CFR 268.40. Inorganic waste containing < 260 ppm non-elemental mercury must be treated by RMERC, and the recovered mercury must be amalgamated. The residues may be disposed of as LLW if they meet the TCLP test limit for mercury (0.20 mg/L), provided that the original waste did not have another RCRA constituent in addition to mercury. If other RCRA constituents were also originally present in the waste above TCLP limits, the waste must be treated to meet the UTS for those constituents, according to 40 CFR 268.48. In the event that the residue does not meet the TCLP limit, it must either be treated again by RMERC (if the residue contains < 260 ppm mercury) to meet the TCLP limit or otherwise treated to meet the UTS (if the residue contains < 260 ppm mercury).

Wastes that originally contained < 260 ppm mercury must be treated to meet the UTS (0.025 mg/L for mercury) for all RCRA constituents, unless RMERC is used, in which case the residue must meet the TCLP limit of 0.20 mg/L for mercury. After treatment to 0.2 mg/L (RMERC residues where mercury is only RCRA constituent) or the UTS (all other situations), the waste may be disposed of as LLW.

Elemental mercury must be treated by amalgamation, after which it may be disposed of as LLW. This applies to original and secondary elemental waste streams.

2.3 What is the Impetus for the Current Study?

2.3.1 Land Disposal Restrictions

The Land Disposal Restrictions (LDR) treatment standards established by the 3rd 3rd Rule (55 FR 2250, June 1, 1990) allows incineration (IMERC) as a treatment option for organic high-mercury wastes. The rationale for this LDR Best Demonstrated Available Technology (BDAT) treatment standard was that incineration most completely destroys the organic component in the waste, allowing recovery of mercury in the incineration residuals. While incineration destroys the organic component of organomercury complexes, it also generates mercury that enters other waste or emissions streams. Since EPA recognizes mercury as a high priority pollutant, it may be preferable to immobilize mercury rather than recover it. Moreover, the EPA has found that most incineration residuals are not treated for mercury recovery.

If a high mercury subcategory waste does not contain organics or is an incinerator or retort residue, the waste is subject to the RMERC treatment standard. Thus, RMERC must be used to treat high mercury subcategory wastes unless the waste contains organics and can be incinerated. In the 3rd 3rd Final Rule, EPA cited Congress' preference for "treatment standards to be based on recovery,

where possible” (S.Rpt. 98-284, p. 17). In addition, the Agency cited technical reasons for not promulgating stabilization as the preferred treatment technology for high mercury subcategory wastes. Specifically, data available to support the 3rd Final Rule indicated that the metal stabilization agents actually increased the mobility of mercury in the stabilized matrix.

2.3.2 Mixed Wastes

The Department of Energy has analyzed the use of the current treatment requirement on radioactive mixed wastes. In 1997, TMFA (then known as the Mixed Waste Focus Area, or MWFA) examined the status of technologies available to treat mercury-contaminated mixed wastes and reported technology shortfalls in a series of technology development requirement documents (TDRDs) for amalgamation, wastes with < 260 ppm mercury, and wastes with \geq 260 ppm mercury. Technology needs were found to exist for mercury stabilization, separation/removal, and amalgamation. The specific technology needs established for mercury and mercury-containing waste were (1) verification of mercury stabilization technology, (2) development of new technology for chemically or physically removing mercury contamination for separate stabilization, and (3) development of methods and equipment designs for amalgamating bulk nonrecyclable mercury. These three goals are summarized in following table.

Table 2-2
Prioritized List of Technology Needs for Mercury
and Mercury-contaminated Wastes

| Technology Need | Description |
|-------------------------------|--|
| 1. Mercury Stabilization | Toxic metal contaminants (regulated under RCRA) contained in mixed wastes require removal or stabilization to control solubility under TCLP conditions before disposal of the wastes is allowed. Under RCRA regulations, waste at contamination levels of <260 ppm mercury (\geq 260 ppm requires retorting) requires stabilization to control mercury solubility to <0.2 ppm. a Verification of treatment (penetrating the entire matrix and stabilizing essentially all of the mercury in the system) is required. |
| 2. Mercury separation/removal | The presence of mercury complicates the design of off-gas systems, the stabilization of residuals, and the monitoring of effluents from thermal systems. Removing the mercury as a pretreatment to simplify downstream operations may be advantageous. New techniques must be developed to remove (physically or chemically) the mercury for separate stabilization. Waste matrices from which mercury separation may be required include soil, all types of process residues or sludges and particulate materials, and debris. Processing methods must ensure adequate removal and must include measuring and monitoring methods to control and verify the process. |
| 3. Mercury amalgamation | Elemental mercury may be derived as a product of retorting waste containing high mercury levels (\geq 260 ppm) or recovered from the off gas of a thermal treatment unit, adding to the elemental mercury streams already in inventory. Radioactive mercury can probably not be completely purified and verified for recycle. Disposal of the mercury will require amalgamation to form a stable, insoluble product. Methods and equipment designs are required for amalgamating bulk nonrecyclable mercury. |

2.4 How Much Waste is There?

Mercury-contaminated wastes in many forms are present at virtually every U.S. Department of Energy (DOE) facility in the United States. In addition to elemental mercury, these waste streams include sludges, soils, and debris waste, with mercury concentrations ranging from < 2 ppm to > 50,000 ppm. Estimates of the inventories of mercury-contaminated, mixed low-level, and transuranic (TRU) wastes in the DOE complex, based on efforts led by the TRU and Mixed Waste Focus Area (TMFA) and its Mercury Working Group (HgWG), are as follows (Conley et al. 1998):

- Approximately 6 m³ of liquid elemental mercury
- Approximately 6,000 m³ of mercury wastes contaminated with < 260 ppm mercury
- Approximately 38,000 m³ contaminated with ³260 ppm mercury and with radionuclides

Additional inventories of elemental mercury will be generated at planned treatment facilities such as the Defense Waste Processing Facility at the Savannah River Site and the Advanced Mixed Waste Treatment Facility at the Idaho National Environmental Engineering Laboratory (INEEL). In addition, treatment of other mercury wastes (e.g., soil, debris) through IMERC and retort RMERC will result in additional volumes of elemental mercury requiring stabilization.

The Department of Energy (DOE) is storing approximately 145 tons of mercury (not including the amount being stored in Y12 for the DLA program). DOE has identified 5 tons of mercury-contaminated wastes currently awaiting disposal as part of an ongoing inventory of such wastes.

2.5 Previous Studies on Treatment of Mercury-Contaminated Wastes

Recognizing the current deficiencies in the current required methods of treatment on radioactive waste contaminated with mercury, the Department of Energy initiated several studies, with EPA's participation. The studies were laid out in a technology development plan, leading to the execution of three technology demonstration campaigns:

- MER01—Demonstration of the Amalgamation Process for Treatment of Radioactively Contaminated Elemental Mercury Wastes
- MER02—Demonstration of the Stabilization Process for Treatment of Radioactively Contaminated Mercury (<260 ppm) Wastes
- MER03—Demonstration of the Stabilization Process for Treatment of Radioactively Contaminated Mercury (≥260 ppm) Wastes

The Transuranic and Mixed Waste Focus Area (DOE) issued solicitations to industry for the MER01 demonstration campaign in November 1996, for MER02 in January 1998, and for MER03 in February 1999 to identify vendors with technologies that could be used to overcome the treatment deficiencies. The goal of the three campaigns is to demonstrate the effectiveness of newly developed technologies that can achieve the following:

- Ensure adequate treatment via amalgamation, stabilization, or thermal treatment
- Include measuring and monitoring methods to control and verify the process
- Minimize worker exposure
- Minimize secondary waste generation
- Maximize operational flexibility and radionuclide containment

The MER01, MER02, and MER03 solicitations targeted the most promising potential treatment technologies for mercury-contaminated wastes. Stabilization is of interest for radioactively contaminated mercury waste (<260 ppm mercury) because of its success with particular wastes, such as soils, and its promise of applicability to a broad range of wastes. For the same reasons, stabilization is also of interest for waste with higher contamination levels (≥ 260 ppm mercury) as a possible alternative to the thermal treatment technologies currently prescribed by law. In either case, however, stabilization methods must be proven to be adequate to meet treatment standards. They must also be proven feasible in terms of economics, operability, and safety. At the time of the solicitations, no standard method of stabilization had been developed and proven for such varying waste types as those within the DOE complex.

2.5 Current Study — Wastes Containing High Mercury (MER04)

The MER04 study is a continuation of the earlier studies of the treatment of mercury-contaminated waste. The MER04 study was initiated and administered by EPA, in consultation with DOE. The study started with a solicitation to industry from January 2001 entitled, “Demonstration Of The Stabilization Process For Treatment Of Mercury Sludge Wastes Containing ≥ 260 ppm Mercury.” This study is designed to supplement the data on treatment of soils, by providing additional data for stabilization of high-mercury subcategory waste sludges. The data gathered from the demonstration of treatment of this sludge should then provide EPA with enough information to support a revision to allow stabilization of all high Hg subcategory wastes. This effort had two major objectives.

1. To evaluate alternative processes to RMERC and IMERC for DOE’s legacy mixed waste. To that end, the processes will treat a high Hg subcategory surrogate waste to meet a TCLP treatment goal of 0.025 mg/L or less. A non-radioactive surrogate waste sludge had been selected to eliminate the added cost and requirements for handling, treatment, and disposal of an actual radioactive mixed waste. The surrogate sludge contained five different forms of mercury including elemental.
2. To provide EPA with the treated waste forms that EPA could test to compare proposed new analytical protocols to the standard TCLP results, and to assess suitable disposal environments for the waste forms. These comparisons will be used by EPA in their efforts to revise the LDR treatment standards for mercury-bearing hazardous wastes.

Technology vendors participated in this demonstration at their expense except for the analytical costs incurred from the use of an outside laboratory to perform the surrogate waste characterization, TCLP testing on the treated waste forms and the costs of shipping the treated waste forms to ALTER, Inc., where the fixed pH leaching was performed and to Oak Ridge National

Laboratory (ORNL) where vapor pressure testing will occur. The results of the Oak Ridge National Laboratory testing will be presented in a separate report. ALTER provided the raw materials and the protocols to make up the surrogate waste.

3. Detailed Description of Study

3.1 Overall Plan

Mercury contamination exists in various forms, such as soil, sludges, and debris, and in various species, such as organic, inorganic, and elemental. The objective of this investigation is to provide information on the ability of current technologies to convert mercury-containing wastes into a stable waste form for disposal. Each of the current technologies relies on chemical reactions to minimize volatilization and solubility, as opposed to recovery or separation technologies which generate a near mercury-free residual in addition to concentrated or purified mercury.

EPA and DOE are investigating possible stabilization methods for mercury-contaminated waste and mixed waste streams. These methods are ‘nonthermal,’ occurring at conditions below the boiling point of mercury (357°C or 675°F). To investigate the ability of these technologies to effectively treat wastes, EPA designed a detailed project plan (EPA Quality Assurance Project Plan — Technical Support for Amendment of Land Disposal Restrictions for Mercury Wastes, December 2000 [QAPP] Appendix A). EPA planned to synthesize a ‘surrogate waste,’ for subsequent treatment by each of several different vendors. This surrogate is intended to be representative of many complex sludges awaiting treatment at DOE facilities. The resulting treated wastes would each undergo a rigorous set of procedures to better understand the performance of the technology. In addition to reducing mercury mobility, the process should minimize worker exposure, minimize volume increase as waste is treated, minimize secondary waste generation, and maximize operational flexibility.

In completing this project, a coordinated effort was required between technology vendors, laboratories, DOE/ORNL, and EPA. Key participants in the project were as follows:

- Treatment technology vendors—Four vendors were selected by EPA as participants in the study. Detailed discussion of their roles, technologies, and activities are discussed in Chapter 4 of this report. Responsibilities of the vendors included receiving the untreated waste components, mixing, treating the surrogate waste using bench scale technology, and sending the treated waste back to the laboratory.
- The Accelerated Life Testing and Environmental Research (ALTER) Corporation, Dillsboro, IN—ALTER’s responsibilities included preparation of the QA plan, preparing the surrogate waste components for distribution to the vendors, receiving the treated wastes, and conducting leaching tests of the resulting treated wastes.
- Environmental Enterprises, Inc., Cincinnati, Ohio—Environmental Enterprise Incorporated was responsible for conducting mercury analysis of solid and aqueous (i.e., leachate) matrices (Appendices B and E).
- Agvise Laboratories, Northwood, ND—Agvise was responsible for testing physical characteristics of the treated waste. These tests include bulk density, moisture content, percent

organic matter, cation exchange capacity, particle size distribution and infiltration rate testing (Appendix C). The Agvise testing uses standard methods for soils, established by the USDA and the Soil Society of America (Appendix D).

- Oak Ridge National Laboratory, Oak Ridge, TN—ORNL was responsible for the measurement of the mercury vapor pressure at 20°C and 60°C of treated waste. ORNL results will be reported separately.

Activities performed by these parties are described below in more detail. These activities include preparing a surrogate sludge for evaluation and treatment and characterizing both the untreated surrogate sludge and treated waste. Activities relating to the treatment itself are discussed in detail in Section 4 of this report.

3.1.1 Surrogate Sludge Preparation

A laboratory scale surrogate mercury sludge was assembled by ALTER for use in this evaluation. The surrogate sludge was intended to be a ‘difficult to treat’ mercury-containing waste representative of the wide range of such wastes that would require treatment. The components of the final surrogate waste included an organic form of mercury (i.e., phenyl mercuric acetate), elemental mercury, and mercury salts (i.e., mercuric chloride, mercuric oxide, and mercuric nitrate) in an inorganic matrix. The overall mercury concentration was 0.5 percent. The sludge composition is outlined in **Table 3-1**. EPA initially considered including a small percentage (1 percent) of motor oil in the surrogate mercury sludge for two reasons: (1) oils may be present in mercury-containing wastes, and (2) the additional oil would be expected to create an even more ‘difficult to treat’ matrix. However, when conducting preliminary testing of such a surrogate waste, EPA could not achieve its performance criteria for mercury analysis. Therefore, motor oil was not part of the final surrogate composition that was sent to vendors for treatment.

The surrogate was shipped as pre-measured components to be blended by the vendors. Vendors were responsible for mixing the surrogate from the components shipped by ALTER.

Table 3-1
Final Surrogate Sludge Composition

| Sludge Constituent | Weight Percent | Mercury Target Concentration, ppm |
|-------------------------|----------------|-----------------------------------|
| Phenyl Mercuric Acetate | 0.08 | 500 |
| Mercury Nitrate | 0.17 | 1000 |
| Elemental Mercury | 0.15 | 1500 |
| Mercury Oxide | 0.11 | 1000 |
| Mercury Chloride | 0.14 | 1000 |
| Diatomaceous Earth | 20 | 0 |
| Aluminum Hydroxide | 10 | 0 |
| Ferric Chloride | 10 | 0 |
| Sodium Chloride | 10 | 0 |
| Water | 49.35 | 0 |
| Total | 100 | 5000 |

3.1.2 Baseline Characterization

ALTER prepared a sample of the waste sludge described above for testing and analysis. The purpose of this was to provide a baseline for comparison with the treated waste received from the vendors. Both the baseline material and the treated wastes obtained from the vendors underwent identical testing and analysis. Deviations between wastes from different vendors or from the baseline are detailed in Section 4 of this report.

At ALTER, sludge was mixed in three-liter batches in a five quart Hobart mixer. Mercury species as listed in Table 3-1 were added only after the major constituents had been well blended. Samples of blended waste were characterized as described in Section 3.2 of this report.

3.1.3 Treated Waste Characterization

Four commercial vendors returned the treated waste to ALTER for testing. The vendor treated wastes were characterized and subjected to physical and chemical analyses to determine their behavior under a range of potential disposal conditions.

3.2 Physical and Chemical Analysis

Samples of the baseline surrogate, the vendor-mixed surrogate before treatment, and the treated waste generated by the vendors were subjected to a battery of physical and chemical analyses. The treatment technologies used by the vendors are described in Section 4. **Table 3-2** summarizes the analyses conducted on the materials.

Table 3-2
Test Procedures for Surrogate Waste Project

| Parameter | Reference | Laboratory | Matrices |
|---|---|---------------------------|------------------------|
| Physical characteristics: density; water content; particle size; infiltration rate; cation ion exchange capacity; percent organic matter; cations (magnesium, potassium, calcium, sodium) | Standard Methods for Soils established by the USDA and the Soil Society of America. | Agvise Laboratories | 1, 2, 3 |
| Mercury analysis, in leachate and solid matrices | SW 846 Method 7470A | Environmental Enterprises | 1, 2, 3; all leachates |
| Mercury vapor pressure testing | Jerome 431 Arizona Instruments (Phoenix, AZ) | ORNL | 3 |
| pH | Standard Methods for the Examination of Water and Wastewater 4500 | ALTER | All leachates |
| Moisture content | ASTM D 2216-80 | ALTER | 1, 3 |
| TCLP leaching | SW 846 Method 1311 | ALTER | 1, 3 |
| Constant pH leaching | QAPP Appendix B | ALTER | 1, 3 |
| Matrices: 1: surrogate waste as mixed by ALTER. 2: untreated waste as prepared by each vendor. 3: treated waste prepared by each vendor. | | | |

In order to assess the stability of the wastes, several leaching procedures were performed on the baseline surrogate and vendor treated waste. Leaching tests performed by ALTER included the toxicity characteristic leaching procedure (TCLP) and constant pH testing. Upon completion of each leaching test, the pH of the leachate was recorded and leachate samples sent to Environmental Enterprises Incorporated for determination of their mercury content. These two leaching tests are discussed below:

- Toxicity Characteristic Leaching Procedure—This is a standard regulatory test (40 CFR 261.24, SW-846 Method 1311) intended to determine the potential mobility of contaminants in a solid waste under simulated landfill conditions. The TCLP entails an initial pH measurement of the waste to determine the appropriate pH of the extraction fluid to be used in at 20:1 liquid/solid ratio (20 Kg/1 L) for a dynamic contact time of 18 hours. The resulting leachate is filtered and analyzed for mercury.

- Constant pH Leaching—Constant pH leaching tests are a means to determine the effect of pH on the stability of a waste. The constant pH procedure was developed by ALTER and is attached as Appendix B to the QAPP (presented in Appendix A of this report). Samples are leached in a constant pH solution that is adjusted to, and maintained at, the desired pH end point. The constant pH leaching tests were performed at pH values of 2, 4, 6, 8, 10 and 12. The pH is maintained by automated systems (designed by ALTER), for a 14 day period, at which point the resulting leachate is filtered and analyzed for mercury. A 20:1 leachate to solids ratio was used in these tests. The longer exposure period of 14 days was selected to ensure equilibrium conditions were obtained.

To assess the effects of grinding to less than 9.5 mm on a macroencapsulated waste form, additional testing was performed on approximately 8 mm cast pellets of two waste forms. Vendor A and Vendor B each submitted two waste forms for testing: (1) crushed material or monolithic material to be crushed, and (2) pelletized material. The pelletized material from Vendor A differed only in size. Vendor B submitted a chemically stabilized crushed material and that same chemically stabilized material macroencapsulated into pellets.

3.3 Selection of Vendors

Four waste treatment technology vendors participated in this study. These vendors were selected jointly between ORNL and EPA. ORNL prepared the statement of work for stabilization vendors and evaluated vendor test plans.

3.3.1 Statement of Work

On January 26, 2001, ORNL issued Request for Proposal (RFP) No. 3400007805. Following evaluation of the proposals, three vendors were initially identified for participation in the study. A fourth participant later asked to participate and became part of the study. The four vendors are identified as vendors A, B, C and D.

ORNL issued contracts with each of the vendors using a statement of work (SOW). The requirements of the vendors expressed in the SOW included the following:

- Types of processes considered—The mercury stabilization process shall stabilize mercury containing wastes without removing the mercury from the waste matrix; processes that involve separating the mercury from the waste matrix followed by amalgamation are not within the scope of the demonstration.
- Effectiveness towards mercury species—The mercury stabilization process must stabilize all forms of mercury including organic and halogenated mercury compounds, elemental mercury, mercury oxides, and mercury nitrates.
- Treatment wastes—The mercury stabilization process should minimize secondary wastes. The waste volume increase of the final waste form due to the stabilization process should also be minimized.
- Effects from heat—During the stabilization process demonstration, a chemical reaction may result that increases the temperature and releases undesired offgases. If this is the case, the demonstration must include control technology to ensure waste integrity and contain both mercury and organic emissions.
- Safety and health—The stabilization process is to accomplish mercury stabilization within the boundaries of worker and public exposure limits as required by OSHA and local radiation control requirements.

Vendors were requested to perform the following activities:

- Prepare a plan
- Prepare/mix surrogate waste using the individual ingredients supplied by ALTER
- Conduct TCLP analysis of the resulting surrogate
- Conduct the treatment using appropriately scaled equipment
- Ship treated waste passing TCLP to ALTER
- Prepare report

3.3.2 Vendor Test Plans

Each vendor was to submit, for review by ORNL, a plan for treatment of the surrogate batches. The plan included the following:

- Mixing method
- Sample containerization and preservation
- Process design and operating data collection
- Total mass of treatment additives

Vendors B and C selected by ORNL and EPA (OSW) received two, pre-measured 50-lb. sets of surrogate sludge components. Vendors A and D each received 1 pre-measured set. Vendors were responsible for mixing the surrogate from the components shipped by ALTER. When mixing was complete, approximately 1 kg of untreated waste, consisting of a composite from approximately 10 random grab samples, was to be collected for shipment to ALTER. Following treatment of each batch, vendors were to submit a sample of each batch to an outside lab for TCLP testing, and return the successfully treated surrogate sludge to ALTER for evaluation and testing.

At ALTER, the treated surrogate was to be crushed if necessary to pass a 9.5 mm sieve. Crushed treated material, or material passing the 9.5 mm sieve was then blended and sub-sampled, using a sample splitter, for each test to be performed.

4. Treatment Technologies

Each of the technologies used by the four vendors involves stabilization of the surrogate sludge. ORNL and EPA specifically were evaluating technologies which immobilize, rather than separate, mercury within wastes. Data and information concerning these treatment technologies were obtained from the vendor project reports submitted to EPA/ORNL, as well as previously prepared technology or performance descriptions prepared for ORNL.

Detailed descriptions of these technologies are presented in this section of the report. Similarities and differences between the technologies are presented in **Table 4-1**.

Table 4-1
Summary of Technologies Used for Surrogate Sludge Treatment

| Comparison Factor | Vendor | | | |
|---|---|--|--|---|
| | A | B | C | D |
| Process Overview* | Formation of mercuric sulfide followed by thermoplastic encapsulation using sulfur polymer stabilization/solidification process | Formation of mercuric sulfide with micro- and macroencapsulation | Amalgamation and stabilization process of elemental Hg followed by precipitation of stable salt. | Formation of mercuric sulfide followed by cement-containing proprietary stabilization agent |
| Reagents Added* | 95% sulfur polymer, 5% organic modifier, and proprietary additives | Sulfide and proprietary binders and coating agents | Amalgamation agent and proprietary precipitation reagent | Sulfide and proprietary cement-containing stabilization agent |
| Waste Loading (on dry basis) | 30 wt% | 72 wt% | Batch 1 44.9 wt% Batch 2 47.0 wt% | 25.4 wt% |
| Volume and/or Weight Increase | 233% by weight on dry basis 36% on volume basis | 38.9% by weight on dry basis | Batch 1 123% by weight Batch 2 113% by weight | 25% by volume 294% by weight |
| Final Form of Treated Waste | Monolithic | Soil-like — Stage 1 Monolithic solid spheres — Stage 2 | Soil-like | Monolithic |
| Mercury Losses to Air | Estimated 0.3% (from historical data) | None identified | Estimated 0.05% | None identified |
| * Several vendors use reagent and/or process steps which have been claimed to be confidential business information (CBI). Only non-CBI is presented in this report. | | | | |

4.1 Treatment of Surrogate—Vendor A

Vendor A used its proprietary sulfur polymer stabilization/solidification (SPSS) process for treating the surrogate waste. The purpose of this process is to chemically stabilize and physically encapsulate mercury to reduce vapor pressure and leachability. This process is conducted in two stages. The first step is a reaction between elemental mercury and mercury compounds, sulfur polymer cement and additives to generate mercuric sulfide (HgS). (Sulfur polymer cement consists of 95 weight percent elemental sulfur reacted with five weight percent of an organic modifier.) During reaction, the vessel is placed under inert atmosphere to prevent mercuric oxide (HgO) formation (a compound much more environmentally mobile than mercuric sulfide) and heated to 40°C to enhance the sulfide formation. The purpose of this first step is to chemically stabilize the mercury. After sulfide formation, the waste is removed.

The purpose of the second step is to solidify the product. The mixture is heated to 130°C to melt the thermoplastic sulfur binder. It is then poured into a mold. On cooling, the reacted sulfide particles become microencapsulated within the monolithic sulfur matrix.

Pilot-scale SPSS processing was accomplished using a 1-ft³, oil-heated, vertical cone mixer. Mixing action is provided by a 24-inch long auger screw. Feed materials were charged to the unit through a 6-inch diameter port on the cone lid with the auger screw drawing material upward from the base of the cone. When mixing, the system was purged with an inert gas by connection to a regulated nitrogen gas supply. Heat was provided to the jacketed cone by a circulating fluid heat transfer system. A heated ball valve at the base of the cone was used to discharge the molten SPSS product.

Off-gas was controlled by a sequence of a heat exchanger, a liquid nitrogen trap, and HEPA/charcoal filters prior to atmospheric discharge. Other than periodic monitoring of the stack gases, Vendor A did not measure mercury air releases during processing of the surrogate sludge. In earlier demonstrations of treatment of elemental mercury and mercury-contaminated soils, a mercury mass balance demonstrated that 0.3% of mercury was volatilized and captured in the offgas collection system.

Each batch of surrogate sludge (batch 1 without Hg, to assess mixing characteristics, and batch 2 with Hg) was prepared in a 45-liter polyethylene container. (Approximately 3 liters of water were kept separate prior to mixing, to use as rinse water, where needed.) The soluble salts (first ferric chloride, then sodium chloride) were dissolved in de-ionized water, followed by addition of the aluminum chloride and diatomaceous earth. The material was mixed with a steel mixing blade. The sludge thickened significantly during addition of the diatomaceous earth. Approximately 15 minutes were required to complete addition of these four major constituents, after which the batches were stirred another 15 minutes to ensure homogenization. The second batch (Batch No. 2) continued to be stirred an additional 15 minutes while the five mercury components were added. The sludge was very corrosive, resulting in severe attack on the mixing blade. The pH of the sludge was measured to be 0.98.

Two 1-liter samples of the mercury-spiked sludge surrogate were collected for bench-

scale process experiments, approximately 5 hours after addition of the mercury compounds. Pre-treatment grab sampling was done several weeks later, just prior to pilot-scale processing. In both cases the sludge was mixed for a minimum of 15 minutes to ensure homogeneity, and was then pumped using a peristaltic pump from the 50-lb batch as it was being mixed.

Vendor A submitted two physical forms of treated waste (both from batch 2) to ALTER for testing. The first waste form was created by allowing the molten material to solidify in bulk. The second waste form submitted for testing by Vendor A was pelletized. To prepare the pellets, monolithic material was heated to approximately 140°C and poured into Teflon molds to create small pellets approximately 8-mm in diameter by 8-mm in length. This dimension was selected so that the material would meet the 9.5 mm particle size requirement for TCLP testing. The bulk (monolithic) material was crushed at ALTER, using a commercial compression machine to yield < 9.5mm pieces for parallel TCLP and constant pH testing. Both the pellet and crushed forms were tested in parallel throughout the evaluation.

4.2 Treatment of Surrogate—Vendor B

Vendor B used a three-step process to stabilize the surrogate. This is a three step process that can be tailored to meet product specification desired by a client. The first step (primary stabilization) involves reaction of the mercury contained in the bulk waste matrix to form a mercuric sulfide product that meets the TCLP UTS for mercury. The second stage of the process involves addition of binders. In the third stage, coating agents are added to render a final waste form that is nominally spherical with a top size diameter of 9.5 mm.

On a dry basis the final product contained 72 wt-% of the surrogate feed material.

4.3 Treatment of Surrogate—Vendor C

Vendor C used an ambient temperature process, developed to treat elemental, ionic, and complexed forms of mercury in mixed (radioactive and hazardous) waste. Vendor C has previously permitted and operated this process for treatment of mercury-contaminated mixed wastes. The surrogate sludge testing was conducted using a pilot-scale reactor capable of handling up to 45-kg of soil and reagents. Test parameters, reagent dosages, and processing equipment were selected based on previous experience. Soil feed and stabilizing reagents were metered directly into the reactor. For mercury-containing wastes, mixing methods become important in dispersing amalgamating/stabilizing reagents to all sites within the matrix that contain the mercury contamination.

Prior to treatment with additives, it is sometimes necessary to condition waste by shredding, grinding, and/or slurring with water. This determination is made based on the capability of the mixing equipment to be used. For the surrogate sludge, Vendor C indicated that pretreatment was necessary but did not identify what type of activity was conducted. Vendor C added only 25% water in assembly of the surrogate, not the 49.35% specified in the instructions.

Two batch runs were performed on the material in aliquots of 50 pounds each. The first

stage of the process involves amalgamation of the elemental mercury component. For matrices such as soil, sulfur is used as the amalgamation agent. The second stage of the process is the stabilization of soluble mercury species using the proprietary reagent. This reagent has the capability to free mercury from stable, soluble complexes and subsequently allow for its precipitation as a stable, non-leachable salt. More specific details on the additives used for the amalgamation or the stabilization step were claimed as confidential business information (CBI).

Following treatment of the surrogate waste, each batch was mechanically discharged from the reactor. The final waste form is best described as a soil-like product containing no freestanding water. The weight of the treated surrogate was increased by about 60 percent. This is much greater than the 15 to 20 percent increase typically seen for soil treated by the process. The difference was potentially due to the extremely high soluble salt content of the surrogate matrix.

During the course of the demonstration, Vendor C also monitored airborne mercury concentrations using a Jerome mercury vapor analyzer. The average mercury concentration measured in the contained work area was at all times less than the American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV) of 0.025 mg/m^3 for mercury vapor. This is the most stringent of applicable enforceable and non-enforceable standards for mercury exposure from ACGIH, the Occupational Safety and Health Administration (OSHA), and the National Institute for Occupational Safety and Health (NIOSH). The reported mercury levels are an average of the room readings (taken from the center of the structure) and an average of the batch mixer readings (taken directly over the batch mixer and in its opening).

These airborne mercury levels were used to estimate the quantity of mercury evolved during processing. Using a conservative flow-rate for the designated containment area, Vendor C estimates that a maximum of 0.05% of the initial inventory of mercury evolved during this demonstration. Therefore, approximately 99.95% of the mercury input to the process was retained within the processing system.

4.4 Treatment of Surrogate—Vendor D

Vendor D treated two 50 pound batches of surrogate material, using the same procedure for each. In making each surrogate batch, Vendor D first mixed the elemental mercury separately with a small quantity of dry ingredients, which were then mixed into the sludge. This was conducted in an effort to better disperse the mercury. After preparation of the sludge, a sulfide solution was added to each 50-lb batch of surrogate material and mixed for 15 minutes. Then, 50 pounds of a proprietary cement containing stabilization agent was added and mixed. Approximately 30 minutes was required for a batch cycle: 5 minutes to pour the sludge into the mixer, 5 minutes to add and mix the sulfide solution, 15 minutes to add and mix the stabilization agent, and 5 minutes to pour the treated waste out of the mixer. Samples for laboratory testing were collected after all stabilization components were mixed in. The remainder of the treated material was poured into a 62-quart cooler lined with a plastic bag (the final volume of the treated material was approximately 2 cubic feet). Temperature increases were observed during

curing. Despite this observation, Vendor D anticipates that temperature control is unlikely to be required during mixing. During curing, temperature control is expected to be adequate if at least one linear dimension of the final waste form is less than 1.5 feet. No data or measurements were available concerning airborne mercury releases during treatment.

The final waste form material in the cooler was cured for one month and then shipped to ALTER, with small samples for vapor testing shipped to Oak Ridge National Laboratory. The consistency of the treated sludge was similar to a pliable clay for one week after treatment, during which the internal temperature remained at about 85°C. After one week the material cooled and set to a very hard concrete. The volume increase resulting from addition of stabilization materials to the surrogate sludge was small, less than 25 percent.

5. Leaching Results

Samples of both the treated and untreated surrogate waste from each vendor were leached according to both the TCLP and the constant pH leaching protocol. Mercury concentrations were measured on the unleached material (untreated surrogate and treated waste forms), and on the leachates generated. Section 5.1 presents the leaching data for the untreated surrogate. Sections 5.2 to 5.5 present the leaching data for the waste forms, by vendor.

5.1 Untreated Surrogate

Table 5-1 summarizes results for total mercury recovered from the digested solids representing the untreated surrogate waste form and the TCLP tests. The amount of mercury recovered from the digested solids is less than the true loading of 5,000 mg/kg, and the standard deviation and coefficient of variation (CV) indicate moderate variation in the measured results. All of the untreated samples fail the TCLP test, as expected for an untreated mercury waste form.

Table 5-1
Analytical Results for the Untreated Surrogate
EEI Work Order 01-05-904

| Sample | Total Hg (mg/kg) | Percent Recovery | Sample | Final pH | TCLP (mg/L) | Percent Leached ¹ | Percent Leached ² |
|-----------|------------------|------------------|-----------|----------|-------------|------------------------------|------------------------------|
| Surrogate | | | TCLP | | | | |
| 1 | 4,660 | 93.2 | 1 | 3.82 | 113 | 45.2 | 56.9 |
| 2 | 3,250 | 65.0 | 2 | 3.65 | 107 | 42.8 | 53.9 |
| 3 | 3,640 | 72.8 | 3 | 3.63 | 111 | 44.4 | 55.9 |
| 4 | 4,090 | 81.8 | 4 | 3.63 | 109 | 43.6 | 54.9 |
| 5 | 4,230 | 84.6 | - | | - | - | - |
| Average | 3,974 | 79.5 | Average | | 110 | 44.0 | 55.4 |
| Std. Dev. | 544 | - | Std. Dev. | | 2.58 | - | - |
| CV | 13.7 | - | CV | | 2.35 | - | - |

¹ Calculated based on the theoretical total mercury content (5000 mg/kg).

² Calculated based on the average total mercury content for the solids.

The amount of mercury recovered by the TCLP test is reported as percent leached, and is based on the average or theoretical mercury concentration for the solid sample. Approximately 50 percent of the mercury is leached from the solid. Percent leached is calculated as follows:

$$[(\text{mg Hg/L leachate})/(\text{mg Hg/kg sample}/20)] * 100$$

where mg Hg/L is the TCLP result, mg Hg/kg sample is the mercury concentration in the solid, and 20 is the liquid/solid ratio of the leaching test. The data are presented based on both the theoretical and measured concentration of mercury in the solid.

Results for the constant pH leach tests are tabulated in **Table 5-2** and plotted on **Figure 5-1** as the concentration of mercury that leached, along with the concentration in the TCLP leachate. The constant pH leaching data are also presented in **Figure 5-2** as the percentage of mercury that leached. Table 5-2 reports the analytical results, the amount of mercury removed from the solid (percent leached), and the total volume of leachate, including the reagents added to maintain the indicated pH. Duplicates were run at pH values of 2, 8, and 12. Relative percent difference (RPD) for the experimental duplicates meet the QA criteria of ± 50 percent. The duplicate values appear with the calculated average on Figures 5-1 and 5-2, and the trend is drawn through the calculated average. Laboratory QA/QC (Appendix E) indicates the analytical results are valid as reported.

Table 5-2
Constant pH Leaching Results for ALTER Constructed Untreated Surrogate
EEI Work Order 01-05-904

| pH | Hg conc. (mg/L) | Percent Leached ¹ | Percent Leached ² | Leachate Volume ³ (mL) | RPD Sample Dups. |
|----|-----------------|------------------------------|------------------------------|-----------------------------------|------------------|
| 2 | 126 | 50.9 | 64.1 | 505.26 | 0.80 |
| 2 | 125 | 50.7 | 63.8 | 507.03 | |
| 4 | 25.7 | 11.2 | 14.1 | 543.94 | |
| 6 | 23.5 | 10.2 | 12.9 | 542.24 | |
| 8 | 22.0 | 9.5 | 12.0 | 540.38 | 14.6 |
| 8 | 19.0 | 7.8 | 9.8 | 514.83 | |
| 10 | 6.66 | 2.9 | 3.7 | 548.01 | |
| 12 | 27.3 | 13.2 | 16.6 | 604.00 | 39.2 |
| 12 | 40.6 | 18.7 | 23.6 | 576.80 | |
| 2 | 0.0520 | - | - | 502.73 | Blank |

¹ Calculated based on the theoretical total mercury content (5000 mg/kg).

² Calculated based on the average total mercury content in the solids.

³ Total volume of leachate, including addition of NaOH and/or HNO₃.

Percent leached is calculated according to the equation presented for the TCLP results, using the leachate volume in Table 5-2 to calculate Liquid/Solid ratio. Values in Table 5-2 indicate a large fraction (up to 63 percent) of the mercury is leached from the solid at pH 2, with moderate amounts of mercury leached over the pH interval of 4 to 12.

Figure 5-1 shows that the percentage of mercury that leached from the sample decreases as pH increases through 10, and then rises as the pH increases to 12. There is little change in the mercury concentration over the pH interval of 4 through 8.

Figure 5-1
Constant pH Leaching Results for ALTER Constructed Untreated Surrogate
Concentration Leached

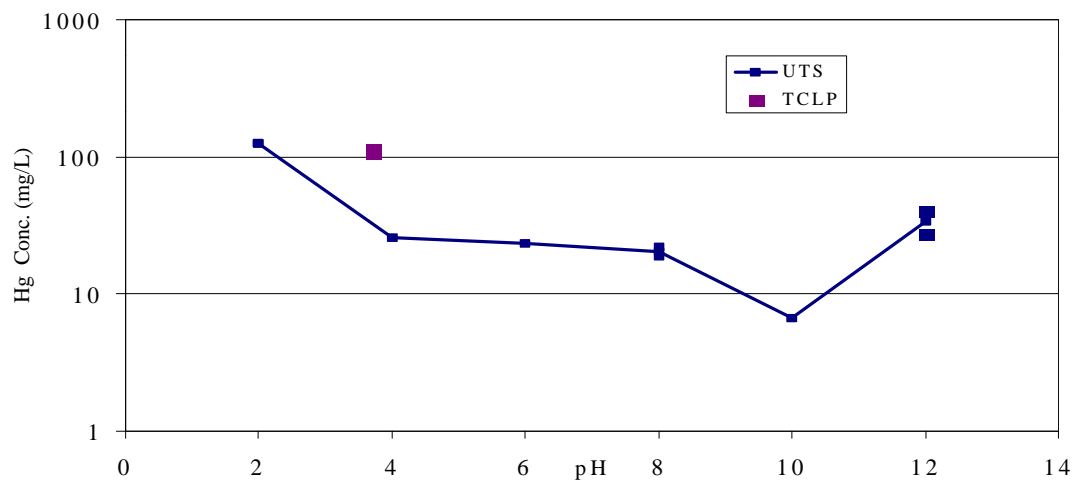
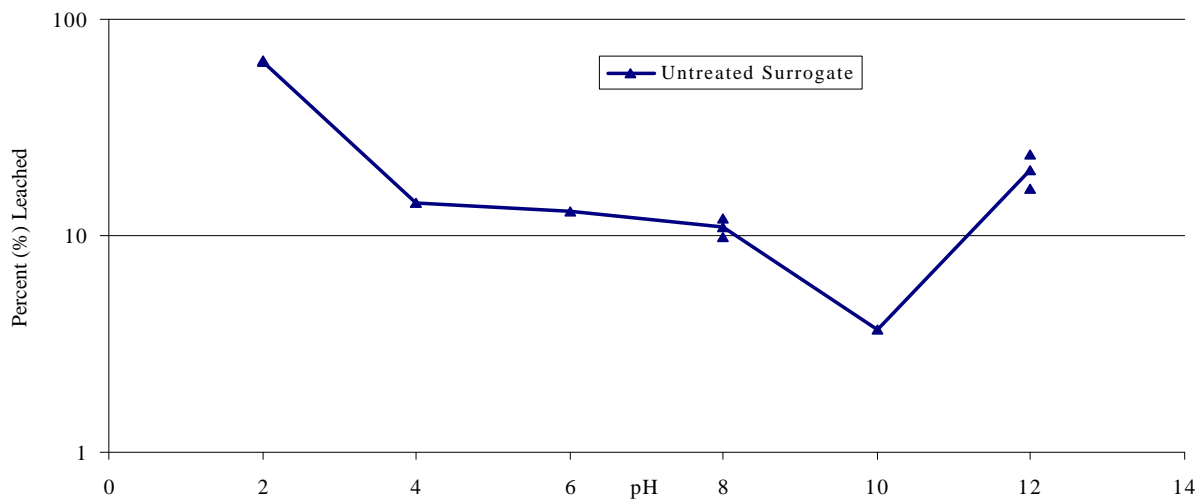


Figure 5-2
Constant pH Leaching Results for ALTER Constructed Untreated Surrogate
Surrogate Percentage Leached



5.2 Vendor A

Table 5-3 summarizes results for total mercury recovered from the digested solids representing the untreated and treated waste form and the TCLP tests. The additives used in the preparation of the treated waste form dilute the untreated surrogate and lower the mercury concentration in the pellets to 2,959 mg/kg, relative to the theoretical value of 5,000 mg/kg for the untreated wet surrogate. The concentration of 2,959 mg/kg is obtained by taking the dry weight basis ⁽¹⁾ of the untreated surrogate (9862 mg/kg) and multiplying it by the surrogate waste loading of 30% ($9862 \times 0.3 = 2959 \text{ mg/kg}$).

Table 5-3
Analytical Results for Vendor A
EEI Work Order 01-10-674

| Waste form | | | TCLP | | | | |
|---------------------|------------------|-------------------------------|-----------|----------|-------------|------------------------------|------------------------------|
| Sample | Total Hg (mg/kg) | Percent Recovery ¹ | Sample | Final pH | TCLP (mg/L) | Percent Leached ¹ | Percent Leached ² |
| Pellets | | | | | | | |
| 1 | 153 | 5.17 | 1 | 4.86 | 0.00116 | 0.000786 | 0.0115 |
| 2 | 73.5 | 2.48 | 2 | 4.91 | 0.00429 | 0.00290 | 0.0426 |
| 3 | 354 | 12.0 | 3 | 4.91 | 0.00223 | 0.00151 | 0.0222 |
| 4 | 243 | 8.21 | 3D | 4.91 | 0.00237 | 0.00160 | 0.0235 |
| 5 | 183 | 6.19 | - | - | - | - | - |
| Average | 201 | 6.80 | Average | - | 0.00251 | 0.00170 | 0.0250 |
| Std. Dev. | 105 | - | Std. Dev. | - | 0.00130 | - | - |
| CV | 52.1 | - | CV | - | 35.9 | - | - |
| Crushed | | | | | | | |
| 1 | 301 | 10.2 | 1 | 4.87 | 0.00266 | 0.00180 | 0.0120 |
| 2 | 312 | 10.6 | 2 | 4.87 | 0.00157 | 0.00106 | 0.00710 |
| 3 | 480 | 16.2 | 3 | 4.81 | 0.00142 | 0.00096 | 0.00642 |
| 4 | 615 | 20.8 | - | - | - | - | - |
| 5 | 504 | 17.0 | - | - | - | - | - |
| Average | 442 | 15.0 | Average | - | 0.00188 | 0.00127 | 0.00851 |
| Std. Dev. | 134 | - | Std. Dev. | - | 0.00068 | - | - |
| CV | 30.3 | - | CV | - | 35.9 | - | - |
| Untreated Surrogate | | | | | | | |
| 1 | 3910 | 78.2 | - | - | - | - | - |
| 2 | 4140 | 82.8 | - | - | - | - | - |
| 3 | 4700 | 94.0 | - | - | - | - | - |
| Average | 4250 | 85.0 | - | - | - | - | - |
| Std. Dev. | 406 | - | - | - | - | - | - |
| CV | 9.56 | - | - | - | - | - | - |

¹ Calculated based on the theoretical total mercury content of 2,959 mg/kg for the pellets.

² Calculated based on the average mercury value reported for the pellets and crushed material.

³ Calculated based on the theoretical mercury content of 5,000 mg/kg for the surrogate.

For the TCLP test, the pellets and crushed fraction show similar results and all results are below the performance goal for the test (i.e., less than 0.025 mg/L). The percentage of material that is leached from the solids is calculated for the theoretical loading of 2,959 mg/kg for the pellets and for the average total mercury value measured on the digested treated solids. The equation used to calculate the values was presented in the preceding section.

Results for the constant pH leach tests are tabulated in **Table 5-4** and plotted on **Figure 5-3** as the concentration of mercury that leached, along with the concentration in the TCLP leachate. The constant pH leaching data are also presented in **Figure 5-4** as the percentage of mercury that leached. Table 5-4 reports the analytical results, the amount of mercury removed from the solid (percent leached), and the total volume of leachate, including the reagents added to maintain the indicated pH. Duplicates were run at pH values of 2, 8 and 11 and 12. Relative percent difference (RPD) for the experimental duplicates do not meet the QA criteria of ± 50 percent, with the exception of the pellet duplicates at pH 12 and the crushed duplicates at pH 8. The duplicate values appear with the calculated average on Figures 5-3 and 5-4, and the trend is drawn through the calculated average. Laboratory QA/QC (Appendix E) indicates the analytical results are valid as reported.

Table 5-4
Constant pH Leaching Results for Vendor A
EEI Work Order 01-10-674

| pH | Pellets | | | | Crushed | | | | RPD Sample Dups. |
|----|-----------------|------------------------------|------------------------------|-----------------------------------|-----------------|------------------------------|------------------------------|-----------------------------------|------------------|
| | Hg conc. (mg/L) | Percent Leached ¹ | Percent Leached ² | Leachate Volume ³ (mL) | Hg conc. (mg/L) | Percent Leached ¹ | Percent Leached ² | Leachate Volume ³ (mL) | |
| 2 | 0.00251 | 0.00170 | 0.0249 | 501.57 | 0.00682 | 0.00461 | 0.0308 | 503.57 | P - 109 |
| 2 | 0.00856 | 0.00579 | 0.0850 | 500.94 | 0.00294 | 0.00199 | 0.0133 | 505.95 | C- 79.5 |
| 4 | 0.00483 | 0.00327 | 0.0480 | 506.40 | 0.00555 | 0.00375 | 0.0251 | 503.40 | |
| 6 | 0.00425 | 0.00287 | 0.0422 | 504.35 | 0.0140 | 0.00946 | 0.0633 | 503.50 | |
| 8 | 0.0127 | 0.00859 | 0.13 | 504.17 | 0.00180 | 0.00122 | 0.0081 | 503.12 | P-99.9 |
| 8 | 0.00424 | 0.00287 | 0.042 | 502.10 | 0.00139 | 0.00094 | 0.0063 | 504.93 | C-25.7 |
| 10 | 0.00734 | 0.00496 | 0.073 | 556.12 | 0.00378 | 0.00256 | 0.0171 | 529.03 | |
| 12 | 0.111 | 0.075 | 1.10 | 504.37 | 0.781 | 0.528 | 3.53 | 550.85 | P-34.3 |
| 12 | 0.157 | 0.106 | 1.56 | 504.72 | 0.136 | 0.0919 | 0.615 | 515.01 | C-141 |
| 2 | <0.00050 | - | - | 501.32 | <0.00050 | - | - | 506.50 | Blank |

¹ Calculated based on the theoretical total mercury content of 2,959 mg/kg for the pellets.

² Calculated based on the average mercury value reported for the pellets and crushed material.

³ Total volume of leachate, including addition of NaOH and/or HNO₃.

Figure 5-3
Constant pH Leaching Results for Vendor A
Concentration Leached

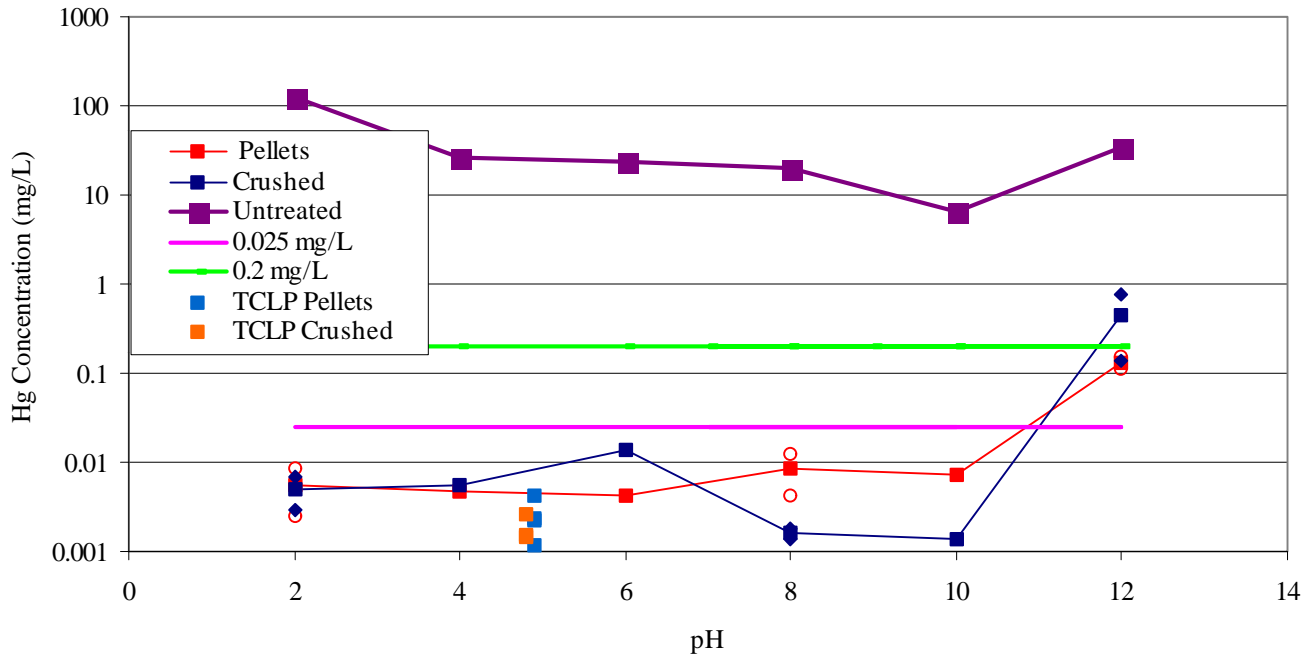
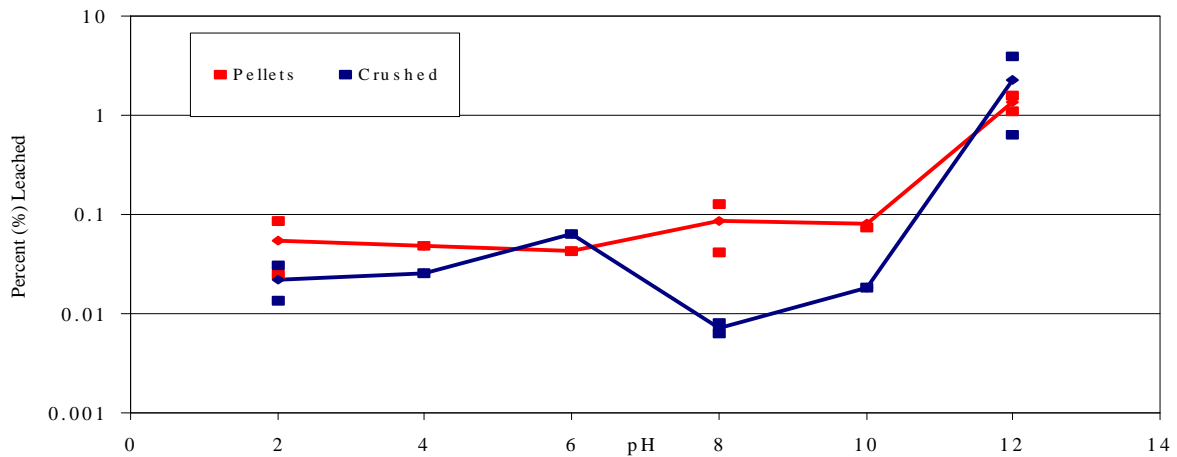


Figure 5-4
Constant pH Leaching Results for Vendor A
Percentage Leached



A comparison of the results for pellets and crushed samples shows that mercury concentrations are similar at pH 2 and 4 and different at pH 6, 8, 10 and 12. Samples representing the pellets show a slow increase in mercury concentration up to pH 10 and then an abrupt increase between pH 10 and 12. The crushed samples show the minimum mercury concentration to lie at pH 8 and 10, and then a sharp jump to the maximum at pH 12.

Percent leached is calculated according to the equation presented for the TCLP results, using the leachate volume in Table 5-4 to calculate Liquid/Solid ratio. Values in Table 5-4 indicate less than one percent of the theoretical mercury loading is released to the solution.

The amount of reagent added to the pH 10 tests was nearly twice as much for the pellet test, relative to the crushed test. There is also an approximate doubling of the observed mercury concentration for the pellet test. A similar pattern is seen for the first pH 12 test. However, when data from all the vendors is examined, there is no clear pattern between the amount of reagent added and the reported mercury concentration.

5.3 Vendor B

Table 5-5 summarizes results for total mercury recovered from digested solids representing an intermediate waste form (Phase I), the final treated waste form (Phase II) and the raw surrogate. The reported standard deviation and CV for the total mercury results are quite low, indicating a good job in the homogenization of the wasteform. Relative to the amount of mercury in the untreated surrogate (5,000 mg/kg wet or 9862 mg/kg dry wt. basis), the mercury surrogate loading of 72% by weight results in a mercury concentration of 7,100 mg/kg ($9862 \text{ mg/kg} \times 0.72$). Note that the vendor prepares the waste on a dry weight basis. Recovery of the mercury from the Phase I waste is nearly twice that of the Phase II material. This implies the digestion used to characterize the mercury loading of the Phase II material was less complete than that carried out on the Phase I waste. In both cases, the digestion did not recover the total mercury loading.

The TCLP tests yielded fairly uniform results for each of the phases, as expected given the uniform recovery on the solids. However, all of the mercury concentrations reported for the TCLP tests did not meet the performance goal for the test (0.025 mg/L). TCLP tests were not performed on the intermediate Phase I solids. The percentage of material that is leached from the solids is calculated for the theoretical loading of 7,100 mg/kg for the Phase I and II solids and for the average total mercury value measured on the digested treated solids.

Table 5-5
Analytical Results for Vendor B
EEI Work Order 01-12-039 & 01-12-515

| Wasteform | | | TCLP | | | | |
|---------------------|------------------|-------------------------------|-----------|----------|-------------|------------------------------|------------------------------|
| Sample | Total Hg (mg/kg) | Percent Recovery ¹ | Sample | Final pH | TCLP (mg/L) | Percent Leached ¹ | Percent Leached ² |
| Phase I Wasteform | | | | | | | |
| 1 | 4,350 | 61.3 | 1 | 5.53 | 0.140 | 0.0394 | 0.0646 |
| 2 | 4,610 | 64.9 | 2 | 5.63 | 0.165 | 0.0465 | 0.0761 |
| 3 | 4,470 | 63.0 | 3 | 5.79 | 0.161 | 0.0453 | 0.0743 |
| 4 | 4,310 | 60.7 | - | | - | - | - |
| 5 | 3,940 | 55.5 | - | | - | - | - |
| Average | 4,336 | 61.1 | Average | | 0.155 | 0.0438 | 0.0716 |
| Std. Dev. | 250 | - | Std. Dev. | | 0.0134 | - | - |
| CV | 5.8 | - | CV | | 8.6 | - | - |
| Phase II Wasteform | | | | | | | |
| 1 | 2,530 | 35.6 | 1 | 4.72 | 0.266 | 0.0749 | 0.201 |
| 2 | 2,690 | 37.9 | 2 | 4.73 | 0.150 | 0.0423 | 0.113 |
| 3 | 2,690 | 37.9 | 3 | 4.73 | 0.112 | 0.0315 | 0.0847 |
| 4 | 2,590 | 36.5 | 4 | 4.73 | 0.107 | 0.0301 | 0.0809 |
| 5 | 2,720 | 38.3 | - | | - | - | - |
| Average | 2,644 | 37.2 | Average | | 0.159 | 0.0447 | 0.120 |
| Std. Dev. | 80.5 | - | Std. Dev. | | 0.07 | - | - |
| CV | 3.04 | - | CV | | 46.6 | - | - |
| Untreated Surrogate | | | | | | | |
| 1 | 6,170 | 123 | - | | - | - | - |
| 2 | 6,930 | 139 | - | | - | - | - |
| 3 | 6,040 | 121 | - | | - | - | - |
| Average | 6,380 | 128 | - | | - | - | - |
| Std. Dev. | 481 | - | - | | - | - | - |
| CV | 7.53 | - | - | | - | - | - |

¹ Calculated based on the theoretical total mercury content of 7,100 mg/kg for the treated waste.

² Calculated based on the average mercury value reported for the Phase I and II material.

³ Calculated based on the theoretical mercury content of 5,000 mg/kg for the surrogate.

Results for the constant pH leach tests are tabulated in **Table 5-6** and plotted on **Figure 5-5** as the concentration of mercury that leached, along with the concentration in the TCLP leachate. The constant pH leaching data are also presented in **Figure 5-6** as the percentage of mercury that leached. Table 5-6 reports the analytical results, the amount of mercury removed from the solid (percent leached), and the total volume of leachate, including the volume of reagents added to maintain the indicated pH. Duplicates were run at pH values of 2, 8 and 11 and 12. Relative percent difference (RPD) for the experimental duplicates meet the QA criteria of ± 50 percent, with the exception of the Phase II sample/duplicate at pH 2. The duplicate values appear with the calculated average on Figures 5-5 and 5-6, and the trend is drawn through the calculated average. Laboratory QA/QC (Appendix E) indicates the analytical results are valid as reported.

Percent leached is calculated according to the equation presented for the TCLP results, using the leachate volume in Table 5-6 to calculate Liquid/Solid ratio. Values in Table 5-6 indicate up to 13 percent of the theoretical mercury loading is released to the solution at pH 2.

Table 5-6
Constant pH Leaching Results for Vendor B
EEI Work Order 01-12-039 & 01-12-515

| pH | Phase I Wasteform | | | | Phase II Wasteform | | | | Memo |
|----|--------------------|---------------------------------|---------------------------------|---|--------------------|---------------------------------|---------------------------------|---|----------|
| | Hg conc. (mg/L) | Percent Leached ¹ | Percent Leached ² | Leachate Volume ³ (mL) | Hg conc. (mg/L) | Percent Leached ¹ | Percent Leached ² | Leachate Volume ³ (mL) | |
| 2 | 46.6 | 13.3 | 21.8 | 507.73 | 1.92 | 0.566 | 1.52 | 523.26 | PI-5.74 |
| 2 | 44.0 | 12.7 | 20.8 | 511.71 | 0.617 | 0.184 | 0.493 | 528.15 | PII-103 |
| 4 | 0.126 | 0.0365 | 0.0599 | 514.92 | 0.137 | 0.0398 | 0.107 | 515.72 | |
| 6 | 0.606 | 0.1808 | 0.2960 | 529.53 | 0.102 | 0.0304 | 0.082 | 529.55 | |
| 8 | 0.344 | 0.0975 | 0.1597 | 503.13 | 0.0873 | 0.0253 | 0.068 | 513.98 | PI-28.9 |
| 8 | 0.460 | 0.1305 | 0.2137 | 503.70 | 0.0753 | 0.0216 | 0.058 | 508.87 | PII-14.8 |
| 10 | 0.0634 | 0.0190 | 0.0311 | 531.84 | 0.0577 | 0.0173 | 0.046 | 531.32 | |
| 12 | 0.0646 | 0.0183 | 0.0299 | 501.61 | 0.00885 | 0.0027 | 0.007 | 548.93 | PI-23.7 |
| 12 | 0.0509 | 0.0175 | 0.0287 | 610.82 | 0.00609 | 0.0019 | 0.005 | 542.26 | PII-36.9 |
| 2 | <0.00050 | - | - | 500.61 | <0.00050 | - | - | 501.40 | Blank |

¹ Calculated based on the theoretical total mercury content of 7,100 mg/kg for the Phase I and II waste.

² Calculated based on the average mercury value reported for the Phase I and II waste.

³ Total volume of leachate, including addition of NaOH and/or HNO₃.

Figure 5-5
Constant pH Leaching Results for Vendor B
Concentration Leached

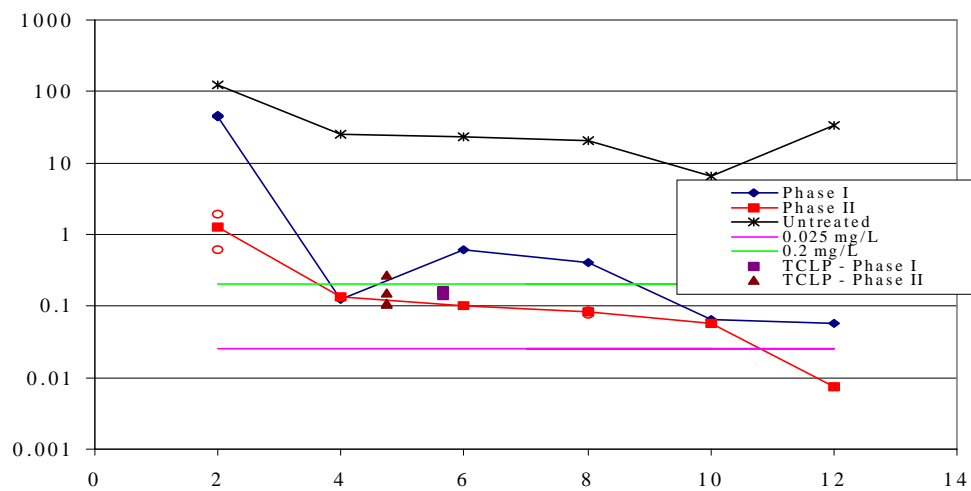
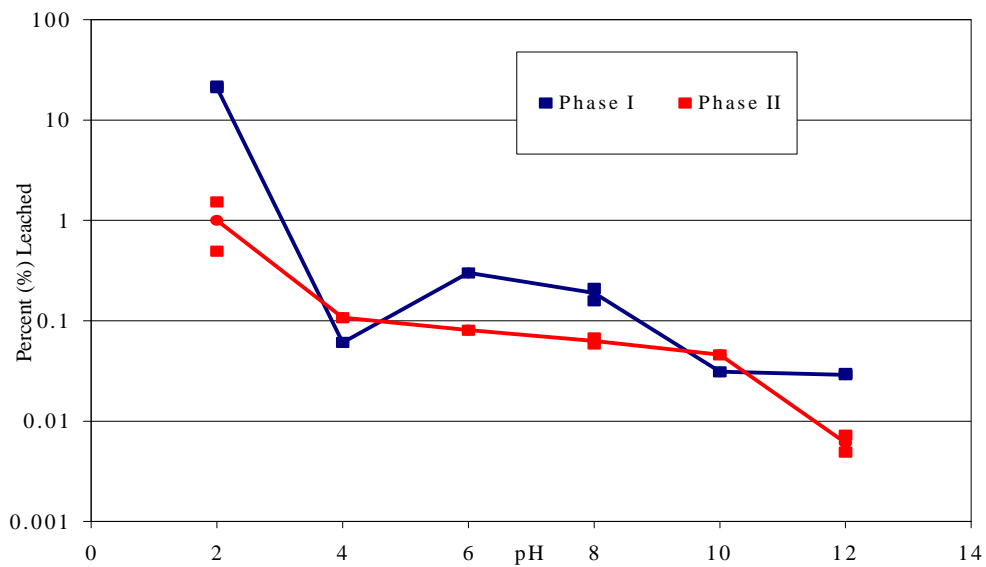


Figure 5-6
Constant pH Leaching Results for Vendor B
Percentage Leached



A comparison of the results for Phase I and Phase II (Figure 5-5) shows that mercury concentrations are similar at pH 4 and 10, but the overall patterns are unique. Samples representing the Phase I material show a sharp decrease from pH 2 to 4 and then an increase to pH 6 followed by a decreasing trend. For Phase II, the mercury concentration steadily decreases as pH increases, with the observed mercury values being about two orders of magnitude lower than the untreated surrogate.

5.4 Vendor C

Table 5-7 summarizes results for total mercury recovered from digested solids representing Batches 1 through 3 and the raw surrogate. The reported standard deviation and CV for the total mercury results are quite low, indicating a good job in the homogenization of the waste form. Relative to the dry weight basis of the raw surrogate (9862 mg/kg) the surrogate loading in batches 1, 2 and 3 was 44.9%, 47% and 31.7%. Therefore, the mercury concentration in waste prepared by Vendor C varies from batch to batch as follows: 4,430 mg/kg (9862×0.449), Batch 1; 4,640 mg/kg, Batch 2; and 3,125 mg/kg, Batch 3. Recovery of the mercury from the waste is nearly identical for Batches 1 and 2 and increases for Batch 3. This implies the digestion used to characterize the mercury loading of Batches 1 and 2 is less complete than that carried out on the Batch 3 waste. In all cases, the digestion did not recover the total mercury loading.

The TCLP tests were performed only on Batch 1 and 2 waste, and the results show greater variability relative to the standard deviation and CV for the total mercury results on the solids. However, all of the mercury concentrations reported for the TCLP tests are less than the performance goal for the test (0.025 mg/L).

The percentage of material that is leached from the solids is very low, and values are calculated for the theoretical mercury loading of each batch and for the average total mercury value measured on the digested treated solids.

Results for the constant pH leach tests are tabulated in **Table 5-8** and plotted on **Figure 5-7** as the concentration of mercury that leached, along with the concentration in the TCLP leachate. The constant pH leaching data are also presented in Figure 5-8 as the percentage of mercury that leached. Table 5-8 reports the analytical results, the amount of mercury removed from the solid (percent leached), and the total volume of leachate, including the total volume of reagents added to maintain the indicated pH. Duplicates were run at pH values of 2, 8 and 11 and 12. An additional set of duplicates was run at pH 2 in an attempt to improve the RPD, but similar results were obtained. Relative percent difference (RPD) for the experimental duplicates at pH 8 (Batch 2 only) and pH 12 meet the QA criteria of ± 50 percent. The duplicate values appear with the calculated average on Figure 5-7 and **Figure 5-8**, and the trend is drawn through the calculated average. Laboratory QA/QC (Appendix E) indicates the analytical results are valid as reported.

Table 5-7
Analytical Results for Vendor C
EEI Work Order 01-08-371 & 01-10-674

| Wasteform | | | TCLP | | | | |
|---------------------|------------------|-------------------------------|-----------|----------|-------------|------------------------------|------------------------------|
| Sample | Total Hg (mg/kg) | Percent Recovery ¹ | Sample | Final pH | TCLP (mg/L) | Percent Leached ¹ | Percent Leached ² |
| Batch #1 | | | | | | | |
| 1 | 1750 | 39.5 | 1 | 8.67 | 0.0102 | 0.00461 | 0.0109 |
| 2 | 1910 | 43.1 | 2 | 8.62 | 0.00945 | 0.00427 | 0.0101 |
| 3 | 1830 | 41.3 | 3 | 8.81 | 0.00769 | 0.00347 | 0.00824 |
| 4 | 1810 | 40.9 | - | | - | - | - |
| 5 | 2030 | 45.8 | - | | - | - | - |
| Average | 1866 | 42.1 | Average | | 0.00911 | 0.00412 | 0.00977 |
| Std. Dev. | 108 | - | Std. Dev. | | 0.00129 | - | - |
| CV | 5.79 | - | CV | | 14.1 | - | - |
| Batch #2 | | | | | | | |
| 1 | 1800 | 38.8 | 1 | 9.14 | 0.000860 | 0.000371 | 0.000933 |
| 2 | 1850 | 39.9 | 2 | 9.10 | 0.00133 | 0.000574 | 0.00144 |
| 3 | 1930 | 41.6 | 3 | 9.12 | 0.00186 | 0.000803 | 0.00202 |
| 4 | 1970 | 42.5 | - | | - | - | - |
| 5 | 1670 | 36.0 | - | | - | - | - |
| Average | 1844 | 39.8 | Average | | 0.00135 | 0.000583 | 0.00146 |
| Std. Dev. | 118 | - | Std. Dev. | | 0.000500 | - | - |
| CV | 6.39 | - | CV | | 37.1 | - | - |
| Batch #3 | | | | | | | |
| 1 | 2170 | 69.4 | - | 6.67 | - | - | - |
| 2 | 2160 | 69.1 | - | 6.67 | - | - | - |
| 3 | 2030 | 65.0 | - | 6.70 | - | - | - |
| 4 | 2090 | 66.9 | - | 6.70 | - | - | - |
| 5 | 2140 | 68.5 | - | | - | - | - |
| Average | 2118 | 67.8 | - | | - | - | - |
| Std. Dev. | 58.1 | - | - | | - | - | - |
| CV | 2.74 | - | - | | - | - | - |
| Untreated Surrogate | | | | | | | |
| 1 | 5790 | 116 ³ | - | | - | - | - |
| 2 | 5340 | 107 ³ | - | | - | - | - |
| 3 | 4720 | 94.4 ³ | - | | - | - | - |
| Average | 5283 | 106 ³ | - | | - | - | - |
| Std. Dev. | 537- | - | -- | - | | | |
| CV | 10.2 | - | - | | - | - | - |
| | | | | | | | |

¹ Calculated based on the theoretical total mercury content of 4,430, 4,640 and 3,125mg/kg for treated waste in Batches 1, 2 and 3, respectively.

² Calculated based on the average mercury value reported for Batches 1, 2 and 3.

³ Calculated based on the theoretical mercury content of 5,000 mg/kg for the surrogate.

Table 5-8
Constant pH Leaching Results for Vendor C
EEI Work Order 01-08-371 & 01-10-360

| pH | Batch #1 | | | | Batch #2 | | | | Memo |
|----|-----------------|------------------------------|------------------------------|-----------------------------------|-----------------|------------------------------|------------------------------|-----------------------------------|---------|
| | Hg conc. (mg/L) | Percent Leached ¹ | Percent Leached ² | Leachate Volume ³ (mL) | Hg conc. (mg/L) | Percent Leached ¹ | Percent Leached ² | Leachate Volume ³ (mL) | |
| 2 | 0.356 | 0.164 | 0.389 | 509.94 | 4.39 | 1.97 | 4.96 | 520.87 | B1-190 |
| 2 | 13.9 | 6.28 | 14.9 | 500.39 | 1.11 | 0.538 | 1.35 | 561.92 | B2-119 |
| 4 | 0.00816 | 0.00377 | 0.0089 | 510.98 | 0.0340 | 0.0158 | 0.0397 | 538.41 | - |
| 6 | 0.0441 | 0.0199 | 0.0653 | 690.76 | 0.118 | 0.0612 | 0.154 | 601.24 | - |
| 8 | 0.0391 | 0.0177 | 0.0426 | 508.74 | 0.0106 | 0.00595 | 0.0149 | 649.94 | B1-62.0 |
| 8 | 0.0206 | 0.00951 | 0.0226 | 511.09 | 0.00797 | 0.00444 | 0.0111 | 644.78 | B2-28.3 |
| 10 | 0.0108 | 0.00497 | 0.0118 | 509.48 | 0.00337 | 0.00149 | 0.0037 | 512.46 | - |
| 12 | 0.0353 | 0.0170 | 0.0404 | 533.58 | 0.00239 | 0.00110 | 0.00279 | 538.25 | B1-4.93 |
| 12 | 0.0336 | 0.01838 | 0.0436 | 605.71 | 0.00264 | 0.00125 | 0.00313 | 547.55 | B2-9.94 |
| 2 | <0.00050 | - | - | 500.58 | <0.00050 | - | - | 500.80 | Blank |
| 2 | 14.9 | 7.11 | 16.9 | 527.64 | - | - | - | - | RB1-188 |
| 2 | 0.478 | 0.217 | 0.514 | 501.98 | - | - | - | - | - |

¹ Calculated based on the theoretical total mercury content of 4,430, and 4,640 mg/kg for treated waste in Batches 1 and 2, respectively.

² Calculated based on the average mercury value reported for Batches 1 and 2.

³ Total volume of leachate, including addition of NaOH and/or HNO₃.

Figure 5-7
Constant pH Leaching Results for Vendor C
Concentration Leached

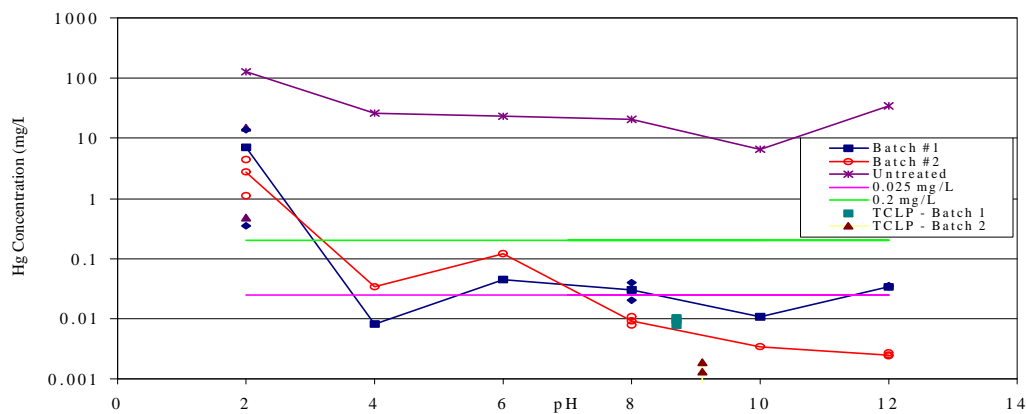
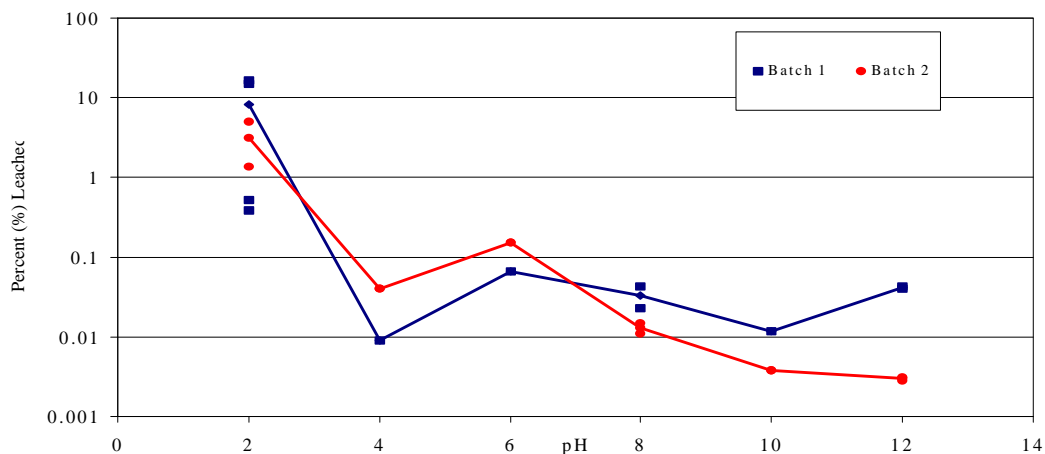


Figure 5-8
Constant pH Leaching Results for Vendor C
Percentage Leached



Percent leached is calculated according to the equation presented previously, using the leachate volume in Table 5-8 to calculate Liquid/Solid ratio. Values in Table 5-8 indicate up to 7 percent of the theoretical mercury loading is released to the Batch 1 solutions at pH 2.

Figure 5-7 compares the results for Batches 1 and 2 and the ALTER untreated surrogate. The plotted mercury concentrations produce similar patterns for each batch, with the exception of the points at pH 12. Samples representing Batch 1 material show an increase at pH 12, relative to a decrease for Batch 2. The minimum mercury concentration is observed at pH 4 for Batch 1 and pH 12 for Batch 2. The observed mercury values are two to three orders of magnitude lower than the untreated surrogate.

5.5 Vendor D

Table 5-9 summarizes results for total mercury recovered from digested solids representing treated material from Batches 1 and 2 and the raw surrogate. The reported standard deviation and CV for the total mercury results indicate moderate variation in the mercury recovered from the waste forms. Relative to the dry weight basis in the untreated surrogate (9862 mg Hg/kg of dry weight), the surrogate loading for batches 1 and 2 was 25.4% by dry weight. Therefore, the mercury concentration in waste prepared by Vendor D is 2,500 mg/kg ($9862 \times .254$). Recovery of the mercury from the waste is similar for Batches 1 and 2, but none of the digestions recovered the total mercury loading.

The TCLP results show greater variability relative to the standard deviation and CV for the total mercury results on the solids. However, all of the mercury concentrations reported for the TCLP tests are less than performance goal for the test (0.025 mg/L), with the exception of Sample 1 in Batch 2.

Table 5-9
Analytical Results for Vendor D
EEI Work Order 01-09-416

| Wasteform | | | TCLP | | | | |
|---------------------|------------------|------------------|-----------|----------|-------------|------------------------------|------------------------------|
| Sample | Total Hg (mg/kg) | Percent Recovery | Sample | Final pH | TCLP (mg/L) | Percent Leached ¹ | Percent Leached ² |
| Batch #1 | | | | | | | |
| 1 | 1210 | 48.4 | 1 | 10.64 | 0.00539 | 0.00431 | 0.00718 |
| 2 | 1530 | 61.2 | 2 | 10.59 | 0.00785 | 0.00628 | 0.0105 |
| 3 | 1280 | 51.2 | 3 | 10.59 | 0.00476 | 0.00381 | 0.00634 |
| 4 | 1630 | 65.2 | 4 | 10.59 | 0.00473 | 0.00378 | 0.00630 |
| 5 | 1860 | 74.4 | - | | - | - | - |
| Average | 1502 | 60.1 | Average | | 0.00568 | 0.00455 | 0.00757 |
| Std. Dev. | 265 | - | Std. Dev. | | 0.00148 | - | - |
| CV | 17.6 | - | CV | | 26.0 | - | - |
| Batch #2 | | | | | | | |
| 1 | 1230 | 49.2 | 1 | 9.14 | 0.0768 | 0.0614 | 0.111 |
| 2 | 1160 | 46.4 | 2 | 9.10 | 0.0119 | 0.00952 | 0.0173 |
| 3 | 1700 | 68.0 | 3 | 9.12 | 0.0578 | 0.0462 | 0.0839 |
| 4 | 1400 | 56.0 | - | | - | - | - |
| 5 | 1400 | 56.0 | - | | - | - | - |
| Average | 1378 | 55.1 | Average | | 0.0488 | 0.0391 | 0.0709 |
| Std. Dev. | 209 | - | Std. Dev. | | 0.0334 | - | - |
| CV | 15.1 | - | CV | | 68.3 | - | - |
| Untreated Surrogate | | | | | | | |
| 1 | 3380 | 67.6 | - | | - | - | - |
| 2 | 3830 | 76.6 | - | | - | - | - |
| 3 | 3910 | 78.2 | - | | - | - | - |
| Average | 3707 | 74.1 | - | | - | - | - |
| Std. Dev. | 286 | - | - | | - | - | - |
| CV | 7.71 | - | - | | - | - | - |

¹ Calculated based on the theoretical total mercury content of 2,500 mg/kg for waste in Batches 1 and 2.

² Calculated based on the average mercury value reported for Batches 1 and 2.

³ Calculated based on the theoretical mercury content of 5,000 mg/kg for the surrogate.

The percentage of material that is leached from the solids is very low, and values are calculated for the theoretical mercury loading of each batch and for the average total mercury value measured on the digested treated solids.

Results for the constant pH leach tests are tabulated in **Table 5-10** and plotted on **Figure 5-9** as the concentration of mercury that leached, along with the concentration in the TCLP leachate. The constant pH leaching data are also presented in Figure 5-10 as the percentage of mercury that leached.. Table 5-10 reports the analytical results, the amount of mercury removed from the solid (percent leached), and the total volume of leachate, including the total volume of reagents added to maintain the indicated pH. Duplicates were run at pH values of 2, 8 and 11 and 12. Relative percent difference (RPD) for the experimental duplicates meet the QA criteria of ± 50 percent, with the exception of the Batch 2 sample/duplicate at pH 2. The duplicate values appear with the calculated average on Figure 5-9 and **Figure 5-10**, and the trend is drawn through the calculated average. Laboratory QA/QC (Appendix E) indicates the analytical results are valid as reported.

Table 5-10
Constant pH Leaching Results for Vendor D
EEI Work Order 01-09-416

| pH | Batch #1 | | | | Batch #2 | | | | RPD Sample Dups. |
|----|--------------------|---------------------------------|---------------------------------|---|--------------------|---------------------------------|---------------------------------|---|------------------------|
| | Hg conc. (mg/L) | Percent Leached ¹ | Percent Leached ² | Leachate Volume ³ (mL) | Hg conc. (mg/L) | Percent Leached ¹ | Percent Leached ² | Leachate Volume ³ (mL) | |
| 2 | 0.127 | 0.1066 | 0.1777 | 525.45 | 0.257 | 0.2348 | 0.427 | 572.06 | B1-48.4 |
| 2 | 0.0775 | 0.0650 | 0.108 | 525.23 | 0.130 | 0.110 | 0.200 | 520.08 | B2-65.6 |
| 4 | 2.63 | 2.61 | 4.35 | 621.42 | 4.35 | 3.67 | 6.67 | 518.48 | |
| 6 | 0.240 | 0.230 | 0.384 | 601.01 | 0.289 | 0.269 | 0.490 | 584.10 | |
| 8 | 0.0603 | 0.056 | 0.0937 | 583.34 | 0.0724 | 0.065 | 0.117 | 558.47 | B1-1.50 |
| 8 | 0.0594 | 0.056 | 0.0937 | 592.18 | 0.0658 | 0.062 | 0.113 | 591.10 | B2-9.55 |
| 10 | 2.17 | 2.16 | 3.60 | 622.85 | 0.0204 | 0.017 | 0.031 | 521.27 | |
| 12 | 0.0156 | 0.0125 | 0.0209 | 502.81 | 0.0250 | 0.020 | 0.037 | 505.47 | B1-35.5 |
| 12 | 0.0109 | 0.0088 | 0.0146 | 503.07 | 0.0193 | 0.015 | 0.028 | 501.11 | B2-43.0 |
| 2 | 0.00052 | - | - | 500.69 | <0.00050 | - | - | 500.51 | Blank |

¹ Calculated based on the theoretical total mercury content of 2,500 mg/kg for waste in Batches 1 and 2.

² Calculated based on the average mercury value reported for Batches 1 and 2.

³ Total volume of leachate, including addition of NaOH and/or HNO₃.

Figure 5-9
Constant pH Leaching Results for Vendor D
Concentration Leached

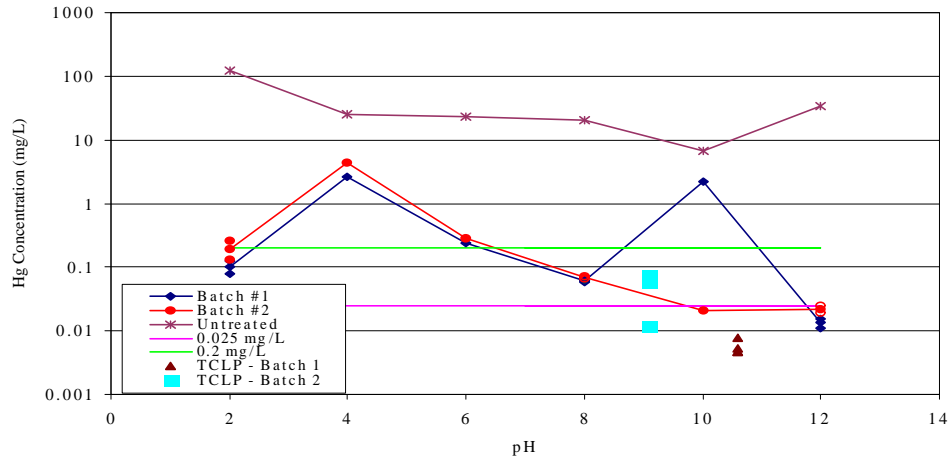
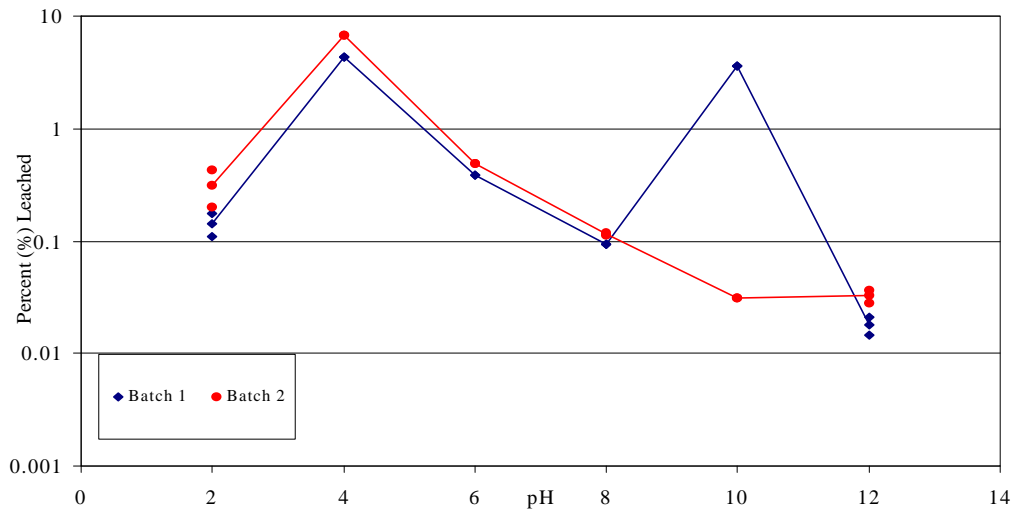


Figure 5-10
Constant pH Leaching Results for Vendor D
Percentage Leached



Percent leached is calculated according to the equation presented previously, using the leachate volume in Table 5-10 to calculate Liquid/Solid ratio. Values in Table 5-10 indicate up to 4 percent of the theoretical mercury loading is released to the Batch 2 solution at pH 4.

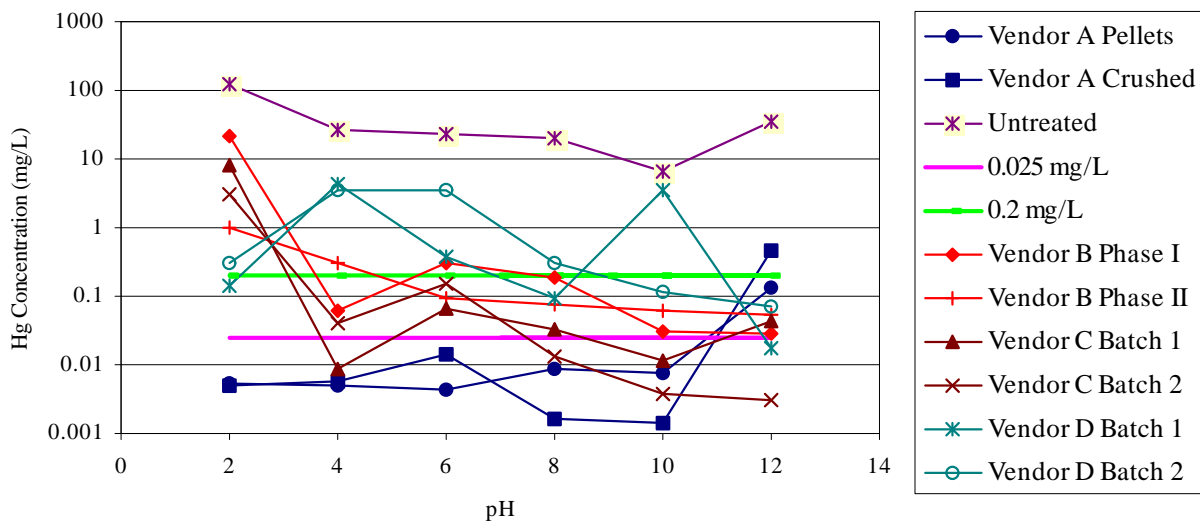
Figure 5-9 compares the results for Batches 1 and 2 and the untreated surrogate. The plotted mercury concentrations produce strikingly similar patterns for each batch, with the exception of the Batch 1 point at pH 10. Although the laboratory QA/QC check corroborates the reported value, it is highly suspect given the excellent agreement of the other samples. However, similar variability was also observed in the region of pH 10-13 in a prior study of soil treated by this process.³ The overall trend is an increase from pH 2 to 4 and a smooth decrease from pH 4 to pH 12. The minimum mercury concentrations are observed at pH 12, and values are one to three orders of magnitude lower than the untreated surrogate.

³ F. Sanchez, D.S. Kosson, C.H. Mattus, and M.I. Morris, Use of a New Leaching Test Framework for Evaluating Alternative Treatment Processes for Mercury Contaminated Mixed Waste (Hazardous and Radioactive); http://www.cee.vanderbilt.edu/cee/research_projects.html

5.6 Conclusions

Figure 5-11 provides the constant pH leach test data discussed previously for all three vendors, plotted on a concentration basis. From this Figure, it is evident that the stability of the mercury in the treated waste forms varies widely across the pH range tested. For example, Vendor A's treated waste form performed better at pH 2 and 10-11, than at the other pHs tested. Vendor B's treated waste form performed best at low pH, while Vendor C's waste form leached less mercury at high pH than at low pH. Clearly, the stability of mercury in these treated waste forms will be highly dependant on the disposal conditions. The combination of site-specific disposal conditions and appropriate treatment technology must be considered as decisions are made about disposal of waste mercury.

Figure 5-11
Constant pH Leaching Results for All Vendors
Concentration Leached



5.7 Additional Information Resources

The following articles are relevant to this topic:

“Stabilization/solidification (S/S) of mercury-containing wastes using reactivated carbon and Portland cement”, Zhang, Jian; Bishop, Paul L. *Journal of Hazardous Materials* (2002), 92(2), 199-212.

“Sulfide-induced stabilization and leachability studies of mercury containing wastes”, Piao, Haishan; Bishop, Paul, *Abstracts of Papers, 223rd ACS National Meeting, Orlando, FL, United States, April 7-11, 2002* (2002), ENV-207.

“Phosphate-induced mercury stabilization”, Zhang, Jian; Bishop, Paul L., *Preprints of Extended Abstracts presented at the ACS National Meeting, American Chemical Society, Division of Environmental Chemistry* (2001), 41(1), 422-424.

“Sulfide-induced mercury stabilization”, Piao, Haishan; Bishop, Paul L., *Preprints of Extended Abstracts presented at the ACS National Meeting, American Chemical Society, Division of Environmental Chemistry* (2001), 41(1), 428-431.

“Stabilization of radioactively contaminated elemental mercury wastes”, Stewart, Robin; Broderick, Tom; Litz, John; Brown, Cliff; Faucette, Andrea., *Proceedings of the International Conference on Decommissioning and Decontamination and on Nuclear and Hazardous Waste Management, Denver, Sept. 13-18, 1998* (1998), 3 33-36.

“Mercury stabilization in chemically bonded phosphate ceramics”, Wagh, Arun S.; Jeong, Seung-Young; Singh, Dileep, *Ceramic Transactions* (1998), 87(Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries III), 63-73.

“A Framework for Risk Assessment of Disposal of Wastes Treated by Solidification/Stabilization”, Batchelor, B., *Environmental Engineering Science*, 14(1): 3-13, 1997.

“A study of immobilization of four heavy metals by solidification/stabilization with Portland cement”, Susan A. Trussell, Ph.D. Dissertation, Texas A&M University, College Station, Texas, 1994.

“Immobilization of chromium and mercury from industrial wastes”, Wasay, S. A.; Das, H. A. , J. *Environ. Sci. Health, Part A* (1993), A28(2), 285-97.

Chemical Fixation and Solidification of Hazardous Wastes, Jesse R. Conner, Van Nostrand Reinhold, New York, 1990.

- “An investigation of mercury solidification and stabilization in portland cement using x-ray photoelectron spectroscopy and energy dispersive spectroscopy”, McWhinney, Hylton G.; Cocke, David L.; Balke, Karl; Ortego, J. Dale., *Cem. Concr. Res.* (1990), 20(1), 79-91.
- “Studies of zinc, cadmium and mercury stabilization in OPC/PFA mixtures”, Poon, C. S.; Perry, R., *Mater. Res. Soc. Symp. Proc.* (1987), 86(Fly Ash Coal Convers. By-Prod.), 67-76.
- “Permeability study on the cement based solidification process for the disposal of hazardous wastes”, Poon, C. S.; Clark, A. I.; Perry, R.; Barker, A. P.; Barnes, P., *Cem. Concr. Res.* (1986), 16(2), 161-72.
- “Mechanisms of metal fixation and leaching by cement based fixation processes”, Poon, C. S.; Clark, A. I.; Peters, C. J.; Perry, R., *Waste Manage. Res.* (1985), 3(2), 127-42.
- “Mechanisms of metal stabilization by cement based fixation processes”, Poon, C. S.; Peters, C. J.; Perry, R.; Barnes, P.; Barker, A. P., *Sci. Total Environ.* (1985), 41(1), 55-71.